of mercuric fluoride was sealed in a closely woven Teflon[23] cloth bag. After it was found that shaking the bag in a bottle did not allow the solid to pass through the interstices of the cloth, the bag was then shaken with anhydrous hydrogen fluoride in a sealed vessel at 100° for 2 hr. The vessel was cooled, the Teflon bag was removed, and the anhydrous hydrogen fluoride was allowed to evaporate to give almost a complete recovery of the mercuric fluoride.

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Friedelin and Related Compounds. VI.[1] Azahomofriedelanes

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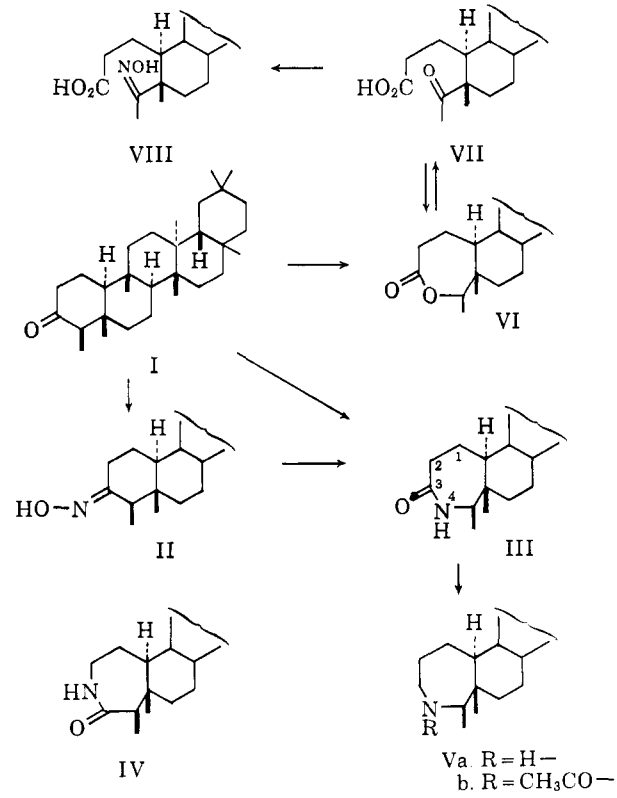
The structure of the product obtained by the Beckmann rearrangement of friedelin oxime (II) and Schmidt reaction of friedelin (I) has been established as 4-aza-A-homofriedelan-3-one (III) by its conversion to the friedelin lactone (VI) by the action of dinitrogen tetroxide.

Considerable work, much of which is reviewed in recent studies,[2-4] has been done on the preparation of azasteroids. The introduction of a nitrogen atom into the steroid ring A to yield the appropriate A-homolactam[3-5] is conveniently accomplished by the Beckmann rearrangement[6] of the easily available 3-ketoximes. Attention has also turned recently to the products obtained by Beckmann rearrangement of the 3-ketoximes[7,8] obtained from triterpenoids (β-amyrin, allobetulin) of the familiar dimethylcyclohexanol ring A structure.

The pentacyclic triterpenoid ketone, friedelin (I), provides a third type of ring A 3-ketone structure. The subjection of friedelin oxime to the action of phosphorus pentachloride in chloroform solution, typical conditions for rearrangement, was reported in 1935 by Drake and Shrader,[9] who established that the product was an "isomeric substance which is no longer an oxime." Their reluctance to formulate this product as a lactam can be attributed to their failure to hydrolyze it under a range of vigorous acid and base conditions or convert it to friedelin or a known derivative. The ready accessibility of friedelin oxime (II) as recently described,[10] has prompted the reinvestigation of this transformation.

Treatment of the oxime (II) with phosphorus pentachloride in chloroform solution gave a product with melting point in agreement with that previously reported,[9] although further purification was effected by chromatographic treatment. The same major product was isolated by the action of *p*-toluenesulfonyl chloride on the oxime in pyridine solution. The infrared spectrum of the product was consonant with an unstrained lactam structure, as expected from a normal Beckmann rearrangement, of which 4-aza-A-homofriedelan-3-one (III) and 3-aza-A-homofriedelan-4-one (IV) are the obvious possibilities. A distinction in favor of III is made on the evidence presented below. Chemical evidence for the presence of the lactam function in III was obtained by reduction with lithium aluminum hydride to give a secondary amine, $C_{30}H_{53}N$, formulated as Va. This yielded, on heating with acetic anhydride, an amide (Vb) whose infrared spectrum lacked an —NH— stretching signal.

Efforts to establish that the lactam had structure (III) by oxidation of the α-methylene group (absent in IV) to yield an α-ketolactam were unsuccessful, unchanged starting material being recovered in high yield after attempted oxidation with selenium dioxide under a variety of conditions[11] and with chromium trioxide in pyridine solution.[12]



The elegant method of conversion of N-alkylamides and lactams to esters and lactones by the action of

(1) Part V, V. V. Kane and R. Stevenson, *Tetrahedron*, **15**, 223 (1961).
(2) T. L. Jacobs and R. B. Brownfield, *J. Am. Chem. Soc.*, **82**, 4033 (1960).
(3) C. W. Shoppee and J. C. P. Sly, *J. Chem. Soc.*, 3458 (1958).
(4) C. W. Shoppee and G. Krueger, *ibid.*, 3641 (1961).
(5) C. W. Shoppee, G. Krueger, and R. N. Mirrington, *ibid.*, 1050 (1962).
(6) L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, **11**, 1–156 (1960).
(7) G. H. Whitham, *J. Chem. Soc.*, 2016 (1960).
(8) J. Klinot and A. Vystrčil, *Collection Czech. Chem. Commun.*, **27**, 377 (1962).
(9) N. L. Drake and S. A. Shrader, *J. Am. Chem. Soc.*, **57**, 1854 (1935).
(10) R. Stevenson, *J. Org. Chem.*, **26**, 2142 (1961).
(11) C. S. Barnes, D. H. R. Barton, J. S. Fawcett, and B. R. Thomas, *J. Chem. Soc.*, 2339 (1952), and M. Falco, W. Voser, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **35**, 2430 (1952), used this oxidation procedure in the lanosterol series.
(12) The use of this reagent to oxidise lactams to α-ketolactams has been demonstrated in the delpheline and aspidospermine alkaloids by R. C. Cookson and M. E. Trevett, *J. Chem. Soc.*, 2689 (1956), and by H. Conroy, P. R. Brooke, and Y. Amiel, *Tetrahedron Letters*, **11**, 4 (1959).

heat on the corresponding N-nitroso derivatives has been reviewed and extended by White.[13] Treatment of the friedelin lactam with dinitrogen tetroxide in carbon tetrachloride at low temperature yielded a lactone, $C_{30}H_{50}O_2$, identified as 4-oxa-A-homofriedelan-3-one (friedelolactone) (VI), thus establishing formulation III for the rearrangement product from friedelin oxime. Initially, the crude nitrosation product was heated in *n*-heptane according to the conditions of White. Subsequently, infrared examination of the crude product showed the absence of lactam and nitroso group, the presence of the carbonyl group and established that the thermal treatment was superfluous. Another example of this lactam → lactone interconversion, where heat treatment is unnecessary, has recently been reported.[14]

The identification of the lactone was made by direct comparison with a product obtained by Baeyer–Villiger oxidation[15,16] of friedelin. Corey and Ursprung[15] treated friedelin with peracetic acid to obtain a lactone mixture which was not separated. In the present work, chromatographic purification of the crude oxidation mixture yielded the lactone identical with that obtained by nitrosation of the lactam. The structure (VI) for the lactone was confirmed by oxidation with chromic acid to yield friedonic acid (VII), further characterized as its methyl ester. The reconversion of friedonic acid to the lactone (VI) either by catalytic hydrogenation or reduction with sodium in *n*-propyl alcohol has been previously described.[17] The hindrance of the ketone group of friedonic acid and the methyl ester has been noted,[17] and no carbonyl derivatives have been previously reported. We find that friedonic acid readily forms an oxime (VIII) under those conditions, refluxing with hydroxylamine hydrochloride in aqueous pyridine, introduced for the characterization of the steroidal hindered 11-ketones.[18]

Friedelin reacted with hydrazoic acid under the usual Schmidt reaction conditions,[19] to give the same lactam (III). The migration of the 4-alkylmethylene group rather than the 2-methylene group is in agreement with the results found for the behavior of 2-alkylcyclohexanones under the same conditions.[20]

The assignment of structure (III) to the lactam indicates that the friedelin oxime described is that geometric isomer with the oxime hydroxyl group *anti* to the equatorial 4-β-methyl group where no pronounced steric effects exist.

Experimental[21]

Beckmann Rearrangement of Friedelin Oxime (II).—(a) Phosphorus pentachloride (1.75 g.) was added to a solution of friedelin oxime (1.74 g.) in chloroform (600 ml.), the mixture allowed to stand at room temperature for 16 hr., then concentrated to a volume of 50 ml. The solution was washed with water, dried (sodium sulfate), concentrated further to 5 ml., and diluted with methanol. The crystalline product (1.30 g., m.p. 312–318°) was collected. Purification by chromatography and elution with ether–methanol (19:1) gave 4-aza-A-homofriedelan-3-one (friedelolactam) (III) as platelets, m.p. 320–324°, $[\alpha]_D$ +11.5° (*c* 2.1), λ^{CHCl_3} 2.96, 3.47, 6.05, 6.89, 7.22, 7.25 (sh.), 7.35, 7.64, 8.56, 8.75, 8.87, 9.90, 10.31 μ (reported,[9] m.p. 316–318°).

Anal. Calcd. for $C_{30}H_{51}ON$: C, 81.57; H, 11.64; N, 3.17. Found: C, 81.32; H, 11.46; N, 3.27.

(b) *p*-Toluenesulfonyl chloride (0.8 g.) was added to a solution of friedelin oxime (630 mg.) in pyridine (40 ml.), the mixture heated on the steam bath for 3 hr., cooled, diluted with water, and extracted with chloroform. The extract was washed with water, concentrated, and diluted with methanol to give the product (310 mg.), m.p. 290–310°, which was chromatographed. Elution with benzene (480 ml.) gave a negligible residue, and with benzene–ether (3:1, 480 ml.) an unidentified solid (60 mg., m.p. 269–278°). Elution with benzene–ether (1:1) then yielded friedelolactam, m.p. 320–323°, $[\alpha]_D$ +11° (*c* 2.0).

The lactam was recovered unchanged after refluxing with selenium dioxide in acetic acid (18 hr.), aqueous acetic acid (2 days), aqueous dioxane (2 days), and benzyl acetate (3 hr.), and treatment with chromium trioxide in pyridine.

Action of Hydrazoic Acid on Friedelin.—Concentrated sulfuric acid (0.2 ml.) was added to a solution of friedelin (213 mg.) in chloroform (8 ml.) cooled in an ice bath. Hydrazoic acid (27 mg.) in chloroform (1.2 ml.) was then added over 15 min., followed by chloroform (3 ml.) containing sulfuric acid (2 drops). After the mixture had been stirred at 0° for 2 hr., it was poured into water, the chloroform layer washed and dried (sodium sulfate), methanol added, and the product recrystallized once to give friedelolactam (140 mg.), m.p. and mixed m.p. 318–319°, $[\alpha]_D$ +10° (*c* 1.5), with infrared spectrum identical with product from Beckmann rearrangement.

4-Aza-A-homofriedelane (Va.)—A solution of friedelolactam (230 mg.) in dry ether–benzene (1:1, 50 ml.) was added to lithium aluminum hydride (600 mg.) in ether (50 ml.), heated under reflux for 3 hr., worked up *via* water and ether extraction to yield a solid (221 mg.) which was recrystallized twice from chloroform–methanol to give 4-aza-A-homofriedelane as soft needles (60 mg.), m.p. 242–244°, $[\alpha]_D$ +8.5° (*c* 1.50), λ^{CHCl_3} 3.45, 6.87, 7.23, 7.35, 8.82, 9.91, 10.90 μ.

Anal. Calcd. for $C_{30}H_{53}N$: C, 84.24; H, 12.49; N, 3.27. Found: C, 84.75, H, 12.23; N, 3.80.

N-Acetyl-4-aza-A-homofriedelane (Vb).—The azahomofriedelane (60 mg.) in acetic anhydride (1 ml.) was heated on the steam bath overnight. On cooling, the mixture solidified, water was added, and the product (m.p. 215–217°) collected. One recrystallization from aqueous methanol gave the acetyl derivative as needles, m.p. 216–217°, $[\alpha]_D$ −30° (*c* 1.50), λ^{CHCl_3} 3.45, 6.19, 6.93, 7.25, 7.46, 7.70, 8.97, 9.35, 9.90, 10.09 μ.

Anal. Calcd. for $C_{32}H_{55}ON$; C, 81.81; H, 11.80; N, 2.98. Found: C, 81.91; H, 11.55; N, 3.31.

Nitrosation of Friedelolactam.—(a) Anhydrous sodium acetate (1.5 g.) was suspended in a saturated solution of dinitrogen tetroxide in carbon tetrachloride (15 ml.) at −60°. A solution of friedelolactam (240 mg.) in carbon tetrachloride (25 ml.) was added dropwise with swirling; the temperature was allowed to rise and was maintained at 0° for 20 min., then room temperature for 20 min. Ice was added to the mixture; the organic layer was separated, washed with water, sodium carbonate solution, and water, dried (sodium sulfate), and evaporated to give a solid which was dissolved in *n*-heptane (75 ml.) and heated under reflux for 16 hr. Removal of the hydrocarbon solvent gave a solid which was crystallized from ethyl acetate to give 4-oxa-A-homofriedelan-3-one (friedelolactone) (VI) as long soft needles (34 mg.), m.p. 306–308° (softens 298°),[22] $[\alpha]_D$ +38° (*c* 1.0), λ^{CHCl_3} 3.43, 5.79, 6.90, 7.22, 7.33, 7.48, 7.54, 7.79, 8.49, 8.78, 9.04, 9.31, 9.76, 10.23 μ.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found, C, 81.64; H, 11.31.

The crystallization residues (92 mg.) were dissolved in benzene and chromatographed to yield a further 50 mg. of the lactone.

(b) In a subsequent experiment, the infrared spectrum of the solid obtained after nitrosation showed absence of the lactam and presence of the lactone carbonyl band. Direct crystallization from ethyl acetate and chloroform–methanol (without heating in *n*-heptane) gave friedelolactone, m.p. 298–300° (softens 290°), $[\alpha]_D$ +40° (*c* 1.2).

(13) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008, 6011, 6014 (1955).
(14) P. Bladon and W. McMeekin, *J. Chem. Soc.*, 3504 (1961).
(15) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **78**, 5041 (1956).
(16) T. Takahashi and G. Ourisson, *Bull. soc. chim. France*, 353 (1956).
(17) N. L. Drake and J. K. Wolfe, *J. Am. Chem. Soc.*, **61**, 3074 (1939).
(18) E. B. Hershberg, E. P. Oliveto, and R. Rausser, *Chem. Ind.* (London), 1477 (1958).
(19) H. Wolff, *Org. Reactions*, **3**, 307–336 (1946).
(20) H. Schechter and J. C. Kirk, *J. Am. Chem. Soc.*, **73**, 3087 (1951).
(21) Melting points were determined on a Gallenkamp melting point apparatus. All specific rotations were measured in chloroform solution. Merck acid-washed alumina was used for chromatography.
(22) Discrepancies in the reported melting point and the dependence on heating rate have been discussed by Takahashi and Ourisson (ref. 16).

4-Oxa-A-homofriedelan-3-one (Friedelolactone) (VI).—Peracetic acid (40%, 7.5 ml.) was added to a solution of friedelin (1.525 g.) in chloroform (70 ml.) and the mixture maintained at 58° for 17 hr. It was then concentrated until solid started to precipitate, methanol added, and the precipitate collected. This was dissolved in benzene, filtered to remove a little insoluble material, washed with water, and concentrated to yield well formed needles (1.34 g., m.p. 279–293°). Chromatography of this product (265 mg.) and elution with benzene (150 ml.) gave a solid (198 mg.) which was recrystallized once from ethyl acetate and once from chloroform–methanol to give friedelolactone as long felted needles, m.p. 303–306° (softens 294°), $[\alpha]_D$ +38° (*c* 1.9), undepressed by specimen obtained from friedelolactam.

Friedonic Acid (VII).—A solution of chromium trioxide (600 mg.) in water (10 ml.) and concentrated sulfuric acid (7.5 ml.) was added to a solution of friedelolactone (550 mg.) in acetic acid (300 ml., freshly distilled from potassium permanganate) and the mixture stirred at room temperature for 16 hr. Methanol was then added, the solution concentrated, diluted with water, and extracted with ether. Sodium hydroxide solution (15%, 200 ml.) was added to precipitate the salt at the interface. Much of the aqueous layer was run off and the ether removed by decantation. The precipitate was washed several times by decantation with water, then warmed on the steam bath to form a gel which gave a granular precipitate on acidification with hydrochloric acid. Two recrystallizations from aqueous ethanol gave friedonic acid (250 mg.) as fine felted needles, m.p. 205–207°, $[\alpha]_D$ −3° (*c* 1.6), λ^{CHCl_3} 2.85, 3.42, 5.88 (broad), 6.85, 7.20, 7.40, 7.79, 8.80 μ (reported,[23] m.p. 206–207°).

Methyl Friedonate.—Excess diazomethane in ether solution was added to friedonic acid (360 mg.) in ether (10 ml.), the solvent removed after 16 hr., and the residual solid crystallized from methanol to yield methyl friedonate as needles (300 mg.), m.p. 155–157°, $[\alpha]_D$ −2° (*c* 1.7), λ^{CHCl_3} 3.42, 5.79, 5.90, 6.88, 7.20, 7.40, 8.55, 8.95, 9.44, 10.10 μ (reported,[24] m.p. 153–154°, $[\alpha]_D$ +12°).

Friedonic Acid Oxime (VIII).—Friedonic acid (260 mg.) was added to a solution of hydroxylamine hydrochloride (355 mg.) in water (1 ml.) and pyridine (8 ml.). After the mixture had been heated under reflux for 20 hr., the solvents were removed under reduced pressure, the residue taken up in ether, washed with water, and dried (sodium sulfate). Removal of the ether gave a solid which crystallized from ethyl acetate to give friedonic acid oxime as stout needles (175 mg.), m.p. 238–240°.

Anal. Calcd. for $C_{30}H_{51}O_3N$: C, 76.06; H, 10.85; N, 2.96. Found: C, 75.43; H, 10.81; N, 2.87.

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(23) N. L. Drake and W. P. Campbell, *J. Am. Chem. Soc.*, **58**, 1681 (1936).

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

The Mutual Decomposition of Benzenesulfonyl Azide and *t*-Butyl Hydroperoxide[1]

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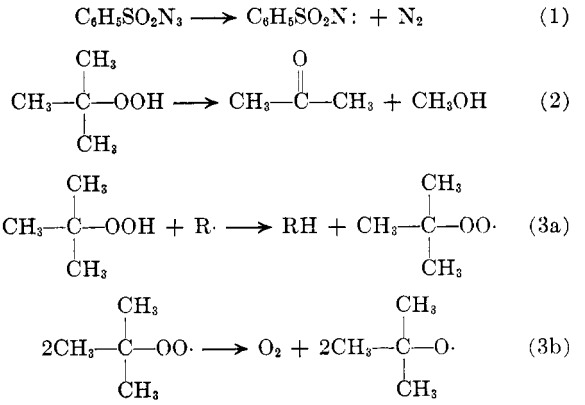
The system benzenesulfonyl azide–*t*-butyl hydroperoxide exhibits mutually induced decomposition of both reagents. The same system in the presence of iodine gives no induced decomposition of the azide, but shows two additional peroxide decomposition reactions, both of which involve both the azide and iodine.

On heating a chlorobenzene solution of benzenesulfonyl azide and *t*-butyl hydroperoxide, intermediates from the decomposing azide induce the decomposition of the peroxide, and intermediates from the peroxide induce the decomposition of the azide. Since a dozen or so different free radicals or diradicals and a correspondingly large number of chain-carrying and chain-breaking steps might plausibly be important in this system, readily interpretable kinetics are not to be expected. We undertook the investigation reported here as the result of a chance observation and were kept from discontinuing it immediately by certain interesting features which we now report.

The decomposition of benzenesulfonyl azide to the nitrene and nitrogen is a well known reaction.[2] It is known both to be accelerated by free radicals[2b] and to induce vinyl polymerization.[2c] The decomposition of *t*-butyl hydroperoxide[3] has two free radical paths, one leading to acetone and methanol, the other to oxygen and *t*-butyl alcohol.

Induced Decomposition of the Azide in the Presence of the Peroxide.—The decomposition of the azide in chlorobenzene at 126.7° can be followed by total gas evolution or by analysis for azide by means of the triphenylphosphine method described in the Experimental. Fig. 1 shows the results of some total gas evolution experiments. The gas evolution rate is equal to that expected from the uncatalyzed azide decomposition at the beginning of the reaction and at the end, but there is an intervening period of very fast nitrogen-plus-oxygen evolution lasting for about forty-five minutes. Extrapolation of the linear portion of the gas evolution curve back to zero time gives an azide concentration considerably less than the actual initial azide concentration. Fig. 2 shows the decrease in azide concentration as determined by the triphenylphosphine



(1) This investigation was supported under a contract with the Office of Naval Research.

(2) (a) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955); (b) M. Takebayashi and T. Shingaki, private communication; (c) J. F. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **82**, 3460 (1960).

(3) (a) B. K. Morse, *ibid.*, **79**, 3375 (1957); (b) V. Stannett and R. B. Mesrobian, *ibid.*, **72**, 4125 (1950); (c) N. A. Milas and D. M. Surgenor, *ibid.*, **68**, 205 (1946).