# Synthesis of Fichtelite and Related Derivatives of Abietane[1]

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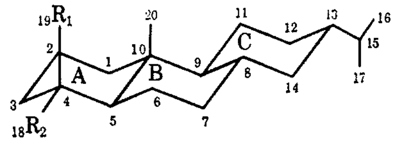
Stereoselective routes to fichtelite (18-norabietane, **1a**) and its C-4 epimer (19-norabietane, **1b**) from abietic acid *via* abietan-18-oic acid (**1c**) are described. The latter acid on conversion into 19-nor-4(18)-abietene (**3**) followed by hydrogenation or hydroboration and reduction yields principally fichtelite, whereas oxidation of the hydroboration product to 18-norabietan-19-al (**1h**) followed by epimerization and reduction affords 19-norabietane. Similar transformations are reported for ring-C aromatic (8,11,13-abietatriene) analogs, together with nmr spectral correlations and a synthesis of the parent hydrocarbon abietane (**1m**).

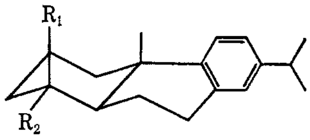
Despite considerable investigation since the isolation of the fossil resin hydrocarbon fichtelite (18-norabietane, **1a**)[3] was reported in 1841,[4] nearly a century elapsed before even the molecular formula, $C_{19}H_{34}$, was established.[5] The apparent origin of fichtelite from abietic-type resin acids, evident from its occurence with the dehydrogenation product retene (1-methyl-7-isopropylphenanthrene),[6] suggested a norabietane structure which was confirmed by X-ray data.[7] However the stereochemistry, particularly at C-4, remained speculative.[8] Some years ago, a total synthesis of a hydrocarbon mixture that may have contained *dl*-fichtelite was reported by Sterling and Bogert.[5]

In the present study, fichtelite and its C-4 epimer **1b** were synthesized stereoselectively from abietic acid (7,13-abietadien-18-oic acid) by reactions which demonstrate that fichtelite has the 4β-methyl configuration shown in **1a**. Subsequent to the preliminary account of our work,[9] Johnson and coworkers[10,11] reported a simplified version of the same route and also a "biogenetic-like polycyclization" leading to *dl*-fichtelite.

In our synthesis, abietan-18-oic acid (**1c**)[12] was converted into 19-nor-4(18)-abietene (**3**), which was then selectively reduced to 18-norabietane (**1a**, fichtelite) or to 19-norabietane (**1b**). Although **1c** can be obtained directly from abietic acid by catalytic hydrogenation over platinum in acetic acid,[12,13] the yield is low and the product is difficult to purify. A more convenient method is by hydrogenation of 8(14)-abieten-18-oic acid, prepared readily by reduction of abietic acid with lithium in ammonia.[12,14]

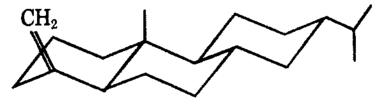


**1**

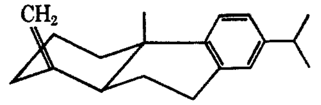


**2**

**a**, $R_1 = CH_3$; $R_2 = H$
**b**, $R_1 = H$; $R_2 = CH_3$
**c**, $R_1 = CH_3$; $R_2 = CO_2H$
**d**, $R_1 = CH_3$; $R_2 = N^+(CH_3)_3I^-$
**e**, $R_1 = CH_3$; $R_2 = N(CH_3)_2O$
**f**, $R_1 = CH_2OH$; $R_2 = H$
**g**, $R_1 = CH_2OTs$; $R_2 = H$
**h**, $R_1 = CHO$; $R_2 = H$
**i**, $R_1 = H$; $R_2 = CHO$
**j**, $R_1 = H$; $R_2 = CH_2OH$
**k**, $R_1 = H$; $R_2 = CH_2OTs$
**m**, $R_1 = R_2 = CH_3$
**n**, $R_1 = CH_3$; $R_2 = CH_2OH$
**p**, $R_1 = CH_3$; $R_2 = CHO$



**3**



**4**

Transformation of **1c** into **3** was patterned after the Hofmann elimination sequence described by Zeiss and Martin[15] for the conversion of dehydroabietic acid (**2c**) *via* methiodide **2d** into the ring-C aromatic analog **4**. Although it has been reported[16] that pyrolysis of N-oxide **2e** offers a superior route to **4**, we found that the original procedure of Zeiss and Martin involving the action of potassium carbonate in refluxing ethanol on methiodide **2d** gave up to 85% over-all yield (from **2c**) of olefinic products containing **4** (*ca.* 80%) and the corresponding 3- and 4-enes (20%). When applied to

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[1] From the Ph.D. Thesis of J. N. M., The University of Kansas, Sept 1965. Financial support for this work from the National Science Foundation (G-19936), The University of Kansas Center for Research in Engineering Science (CRES-40B), and the Alfred P. Sloan Foundation is gratefully acknowledged.

[2] (a) Alfred P. Sloan Research Fellow, 1961-1964. (b) Predoctoral Fellow, U. S. Public Health Service, 1964-1965.

[3] (a) The abietane numbering and systematic nomenclature follow recent proposals (third revision, Oct 1968) of a group chaired by Dr. J. W. Rowe, U. S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis. (b) *Cf.* R. McCrindle and K. H. Overton, *Advan. Org. Chem.*, **5**, 50 (1965). (c) See also E. Fujita, T. Fujita, and H. Katayama, *Chem. Commun.*, 968 (1967); Abstracts of Papers, 5th International Symposium on the Chemistry of Natural Products, London, July 8-13, 1968, p 323.

[4] C. Bromeis, *Ann.*, **37**, 304 (1841).

[5] For review, see E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939); see also, J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, University Press, Cambridge, England, 1952, pp 337-338. For recent work on the occurrence of fichtelite, see papers by A. I. Skrigan cited in *Chem. Abstr.*, **55**, 18889*e* (1961); **62**, 10664*a* (1965).

[6] L. Ruzicka and E. Waldmann, *Helv. Chim. Acta*, **18**, 611 (1935).

[7] D. Crowfoot, *J. Chem. Soc.*, 1241 (1938); *cf.* H. Strunz, *Naturwissenschaften*, **49**, 9 (1962).

[8] L. F. Fieser and M. Fieser, "Topics in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1963, p 199.

[9] A. W. Burgstahler and J. N. Marx, *Tetrahedron Lett.*, 3333 (1964).

[10] N. P. Jensen and W. S. Johnson, *J. Org. Chem.*, **32**, 2045 (1967). We are grateful to Professor Johnson and Dr. Jensen for sending us a copy of their paper prior to publication.

[11] W. S. Johnson, N. P. Jensen, and J. Hooz, *J. Amer. Chem. Soc.*, **88**, 3860 (1966); W. S. Johnson, N. P. Jensen, J. Hooz, and E. J. Leopold, *ibid.*, **90**, 5872 (1968).

[12] A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *J. Org. Chem.*, **34**, 1550 (1969); *cf.* J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *ibid.*, **31**, 4128 (1966). We thank Professors Huffman and Herz for sending us a copy of their manuscript before publication.

[13] L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, **5**, 315 (1922).

[14] E. E. Royals, W. C. Bailey, and R. W. Kennedy, *J. Org. Chem.*, **23**, 151 (1958); R. W. Kennedy, Ph.D. Thesis, Emory University, 1957; University Microfilm 58-5153.

[15] H. H. Zeiss and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **75**, 5935 (1953); *cf.* A. W. Burgstahler, Ph.D. Thesis, Harvard University, 1952.

[16] J. W. Huffman and R. F. Stockel, *J. Org. Chem.*, **28**, 506 (1963).

TABLE I

PROTON CHEMICAL-SHIFT VALUES FOR ABIETANE AND 8,11,13-ABIETATRIENE DERIVATIVES[a]

| Abietane series | | | 8,11,13-Abietatriene series | | |
|---|---|---|---|---|---|
| Compd | C-10 methyl, τ | Other peaks,[b] τ (J, Hz) | Compd | C-10 methyl, τ | Other peaks,[c] τ (J, Hz) |
| **1a** | 9.18 | C-4 methyl at 9.05 (d, $J = 4$) | **2a** | 8.83 | C-4 methyl at 8.96 (d, $J = 7$)[d] |
| **1b** | 9.25 | C-4 methyl at 9.10 (d, $J = 3$) | **2b** | 8.89 | C-4 methyl at 9.03 (d, $J = 5$)[d] |
| **1f** | 9.33 | $CH_2OH$ at 6.40 ($W_{1/2} = 10$) | **2f** | 8.97 | $CH_2OH$ at 6.28 ($W_{1/2} = 11$) |
| **1g** | 9.35 | $CH_2OTs$ at 6.00 ($W_{1/2} = 16$) | **2g** | 8.98 | $CH_2OTs$ at 5.92 ($W_{1/2} = 16$) |
| **1h** | 9.32 | CHO at −0.20 (d, $J < 1$) | **2h** | 8.97 | CHO at −0.21 (d, $J < 1$) |
| **1i** | 9.20 | CHO at 0.37 (d, $J = 3$) | **2i** | 8.86 | CHO 0.26 (d, $J = 3$) |
| **1j** | 9.22 | $CH_2OH$ at 6.41 ($W_{1/2} = 6$) | **2j** | 8.87 | $CH_2OH$ at 6.31 ($W_{1/2} = 5$) |
| **1k** | 9.27 | $CH_2OTs$ at 6.00 ($W_{1/2} = 8$) | **2k** | 8.92 | $CH_2OTs$ at 5.93 ($W_{1/2} = 7$) |
| **1m** | 9.17 | C-4 methyls at 9.15, 9.16[e] | **2m** | 8.84 | C-4 methyls at 9.05, 9.05[f,g] |
| **1n** | 9.16 | $CH_2OH$ at 6.85 (q, $J = 10$), C-4 methyl at 9.25 | **2n** | 8.83 | $CH_2OH$ at 6.80 (q, $J = 11$), C-4 methyl at 9.18 |
| **1p** | 9.12 | CHO at 0.85, C-4 methyl at 8.96[e] | **2p** | 8.80 | CHO at 0.73, C-4 methyl at 8.86[f] |

[a] Determined in carbon tetrachloride solution on a Varian A-60 or HA-100 nmr spectrometer with tetramethylsilane as internal reference. [b] Isopropyl doublet centered at τ 9.14 ± 0.02 ($J \sim 5.5$–7.0 Hz). [c] Isopropyl doublet centered at τ 8.78 ± 0.02 ($J \sim 6$–7 Hz). [d] Similar values have been found for the corresponding nor-8,11,13-podacarpatriene by J. dePaiva Campello (M.S. Thesis, Indiana University, June 1966). We cordially thank Professor Ernest Wenkert for this information. [e] *Cf.* ref 3c. [f] *Cf.* ref 23. [g] Prepared from **2c** essentially by the method of W. P. Campbell and D. Todd, *J. Amer. Chem. Soc.*, **64,** 928 (1942); *cf.* E. Wenkert, P. Beak, R. W. J. Carney, J. W. Chamberlin, D. B. R. Johnston, C. D. Roth, and A. Tahara, *Can. J. Chem.*, **41,** 1924 (1963); glpc, $r_{\text{Pim}}$ (see ref 25) = 0.55.

acid **1c,** the sequence afforded **3** of comparable purity in 70% over-all yield.[17]

By analogy with similar structures,[18] **3** would be expected to undergo hydrogenation predominantly from the α side to produce the axial 4β-methyl product **1a.** In fact, hydrogenation of **3** over platinum in acetic acid afforded a mixture containing mostly **1a,** which was shown to be identical with a sample of natural fichtelite.[19] To confirm the 4β-methyl configuration of fichtelite, the 4α-methyl epimer **1b** was prepared. Hydroboration–oxidation of olefin **3** gave mainly 18-norabietan-19-ol (**1f**) plus some fichtelite, evidently by protonolysis of the intermediate organoborane.[20] Subsequent conversion of **1f** into fichtelite by tosylation to **1g,** displacement with *n*-butyl mercaptide, and desulfurization demonstrated that both hydrogenation and hydroboration of **3** follow the same stereochemical course. The axial configuration of the C-4 substituent was assigned on the basis of the fact that mild oxidation of **1f** with Jones reagent[21] gave an aldehyde (**1h**) which was isomerized by acid to the equatorial 4α epimer **1i.** The two aldehydes, **1h** and **1i,** were found to have readily distinguishable nmr spectra (Table I), and each was uncontaminated with the other within the limits of detectability.

A mixture of **1h** and **1i,** along with other products, resulted from boron trifluoride rearrangement of the epoxide prepared by the action of *m*-chloroperbenzoic acid on **3.** Wolff–Kishner reduction of **1i** or, alternatively, its reduction to alcohol **1j,** followed by conversion into the tosylate (**1k**) and the *n*-butyl thio ether, and desulfurization then furnished hydrocarbon **1b.** The latter, obtained as an oil, $[\alpha]_D$ +5°, has infrared (ir) and nmr spectra that are different from those of fichtelite. In particular, the C-10 methyl signal appears at higher field in the nmr spectrum (Table I) of **1b** than it does in that of **1a,** as would be expected for relief of the 1,3-diaxial interactions present in **1a** but not **1b.**[22,23] Thus it is firmly established that fichtelite is 18-norabietane (**1a**) and that its formation in nature by reduction and decarboxylation of abietic-type resin acids[5] occurs with retention of the β-methyl configuration at C-4.

In the 8,11,13-abietatriene series, hydrogenation of olefin **4** similarly furnished predominantly the 4β-methyl epimer **2a,** as judged by the nmr spectrum (Table I). Nitration gave a ring-C dinitro derivative not identical with that (mp 133–134°) obtained by Perold and Jeger[19b] from fichtelite by partial dehydrogenation and subsequent nitration. This result implies that the stereochemistry of their product differs from that of the parent hydrocarbon.

Application of the hydroboration–isomerization–reduction sequence to **4** gave the 4α-methyl hydrocarbon **2b,** whose ir spectrum differs markedly from that of **2a** but corresponds closely to that of the dehydrogenation product of fichtelite published by Perold and Jeger.[19b]

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(17) An alternative, one-step route to **4** by treatment of **2c** with lead tetraacetate has been reported [J. W. Huffman and P. G. Arapakos, *ibid.*, **30,** 1604 (1965)], but we found the reaction to be rather unselective, with **4** constituting less than half of the olefinic products. Jensen and Johnson,[10] however, successfully utilized this method in their synthesis of fichtelite from 8(14)-abieten-18-oic acid. Recently, nitrous acid deamination of 4α-amino-18-nor-8,11,13-abietatriene has been reported [R. N. Seelye and W. B. Watkins, *Tetrahedron Lett.*, 1271 (1968)] to give a 45% yield of alkenes containing 65% **4,** whose nmr spectrum is also recorded by these authors.

(18) *Inter alia,* J. A. Marshall and N. Cohen, *J. Amer. Chem. Soc.*, **87,** 2773 (1965); A. S. Bawdekar and G. R. Kelkar, *Tetrahedron*, **21,** 1521 (1965). An example of the opposite result has been reported for a 4-methylene-9β,-19-cyclosteroidal alkaloid [K. S. Brown, Jr., and S. M. Kupchan, *J. Amer. Chem. Soc.*, **86,** 4430 (1964)], but molecular models show that the compound has a conformation quite different from that of **3.**

(19) (a) We cordially thank Professor O. Jeger for this sample of natural fichtelite. (b) *Cf.* G. W. Perold and O. Jeger, *Helv. Chim. Acta*, **32,** 1085 (1949).

(20) This side reaction is not normally encountered in a basic peroxide medium. *Cf.* H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 62–66. It should also be noted that treatment of the organoborane with acetic or propionic acid yielded little or no hydrocarbon.

(21) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(22) G. Slomp, Jr., and B. R. McGarvey, *J. Amer. Chem. Soc.*, **81,** 2200 (1959).

(23) The opposite effect observed in the spectra of the C-4 epimeric oxygenated derivations (*e.g.*, **1f–l**) is also as expected: E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30,** 713 (1965), and pertinent references cited therein. See also J. W. ApSimon, P. V. Demarco, D. W. Mathieson, and W. B. Whalley, *Tetrahedron*, **23,** 2375 (1967); C. R. Narayana and N. K. Venkatsubramanian, *Tetrahedron Lett.*, 3639 (1965); C. R. Narayanan and N. R. Bhadane, *ibid.*, 1565 (1968).

The dinitro derivative of **2b** prepared on one occasion had mp 151–153°, but in other preparations it had mp 130–131°.[24] The latter is in agreement with the melting point reported by Perold and Jeger for their dinitro derivative, indicating that epimerization had occurred at C-4 in their aromatization of ring C of fichtelite.

Incidental to the synthesis of fichtelite, we also prepared the "parent" hydrocarbon abietane (**1m**), mp 38–38.5°, by reduction of acid **1c** to abietan-18-ol (**1n**), oxidation to aldehyde **1p**, and Wolff–Kishner reduction. This same route has since been reported by Fujita and coworkers[3c] in connection with their studies on the structure and chemistry of the diterpene enmein.

## Experimental Section[25]

**19-Nor-4(18)-abietene (3).**—The preparation of this olefin on a 1-g scale from **1c**, mp 181–182°[12] (preferably purified through the methyl ester, mp 45–46°[12,26]), was patterned after "Method a" of Zeiss and Martin[15] for the analogous conversion of **2c** into **4**. The intermediate base, **4α-methylamino-18-norabietane,** was characterized as the **hydrochloride,** mp 265–265.5° dec, after recrystallization from ethanol–ethyl acetate.

*Anal.* Calcd for $C_{20}H_{38}ClN$: C, 73.24; H, 11.37; Cl, 10.81. Found: C, 73.29; H, 11.40; Cl, 10.40.

Crude **3** from the Hofmann elimination was obtained as an oil in 70% over-all yield from acid **1c**. Although the ir spectrum showed the expected exocyclic methylene absorption at 6.1 and 11.2 μ, glpc and nmr analysis indicated that it was a mixture of double-bond isomers containing *ca.* 80% **3**. The major contaminant appeared to be 19-nor-3-abietene (nmr signal at $\tau$ 4.75; glpc $r_{\mathrm{Pim}}$ 0.40). Chromatography on silver nitrate impregnated alumina[12] and elution with petroleum ether–ether (10:1) furnished a homogeneous sample of **3**: glpc $r_{\mathrm{Pim}}$ 0.42; $[\alpha]_D$ +66°; $n^{25}_D$ 1.5102; and principal nmr peaks at $\tau$ 5.25, 5.51 (=$CH_2$), 9.14 (d, $J$ = 6.5 Hz, isopropyl), and 9.33 (shielded C-10 methyl).

*Anal.* Calcd for $C_{19}H_{32}$: C, 87.62; H, 12.38. Found: C, 87.45; H, 12.27.

Olefin **3** was also prepared by the method of Huffman and Stockel,[16] but the yield was lower. Cope elimination of amine oxide **1e** was extremely facile and occurred largely during formation. The tertiary base, **4α-dimethylamino-18-norabietane,** was characterized as the yellow **picrate,** mp 192–193°, after recrystallization from ethanol–ether.

*Anal.* Calcd for $C_{27}H_{42}N_4O_7$: C, 60.65; H, 7.92; N, 10.48. Found: C, 60.64; H, 7.74; N, 10.20.

**18-Norabietane (Fichtelite, 1a). A. By Hydrogenation.**—A solution of 0.50 g (1.9 mmol) of crude **3** in 15 ml of acetic acid was stirred at 25° with 0.1 g of prereduced platinum oxide under 1 atm of hydrogen. After 10 min, the reaction was complete, and the product was recovered by extraction and passage through alumina with petroleum ether. When seeded in methanol with natural fichtelite,[19] it gave 230 mg (44%) of elongated plates or flattened needles of **1a**: mp 32–37° (after four crystallizations the melting point was 42–45°; after four more it was 45–46°); $[\alpha]_D$ +19° (lit. mp 46°, $[\alpha]_D$ +18°;[5] mp 45.8–46.1°, $[\alpha]_D$ +19°[10]); ORD ($c$, 0.10 in hexane) $[\Phi]_{400}$ +80°, $[\Phi]_{300}$ +280°, $[\Phi]_{250}$ +400°, $[\Phi]_{225}$ +825°. The mixture melting point with authentic fichtelite was 45–46°. The ir spectrum (solution and KBr disk), nmr spectrum (Table I), X-ray powder diffraction pattern,[27] and glpc behavior ($r_{\mathrm{Pim}}$ 0.36) were identical with those of natural fichtelite.

*Anal.* Calcd for $C_{19}H_{34}$: C, 86.94; H, 13.06. Found: C, 87.23; H, 12.74.

**B. By Hydroboration.**—To an ice-cold solution of 0.35 g of lithium aluminum hydride and 1.11 g (4.23 mmol) of crude **3** in 25 ml of dry ether was added 1.2 ml of boron trifluoride etherate in 20 ml of ether over a period of 30 min. The mixture was stirred for 2 hr at 25° and then treated with saturated sodium sulfate solution and solid anhydrous sodium sulfate. The solids were separated and the ether replaced by 40 ml of tetrahydrofuran. To the resulting solution 20 ml of 10% sodium hydroxide and 15 ml of 30% hydrogen peroxide were added, and the two phases were stirred rapidly for 5 hr at 25°. After dilution with water and extraction with ether, the mixture furnished 1.10 g of an oily product which was chromatographed on 30 g of silica gel (Grace, 100 mesh, activated). Elution with petroleum ether–benzene (2:1) afforded 0.17 g (15%) of hydrocarbon mixture, $R_f$ 0.80 (6:1), whose recrystallization behavior and analysis by glpc and nmr showed that it was mainly fichtelite. Direct hydrolysis of the organoborane product with acetic acid or propionic acid was unsuccessful. **18-Norabietan-19-ol (1f),** undoubtedly containing minor amounts of product derived from isomeric contaminants in **3,** was eluted from the column with benzene–ether (19:1) as a viscous oil: yield 0.91 g (77%); $R_f$ 0.26 (6:1); ir bands at 2.8 and 3.0 μ. This product was characterized by its nmr spectrum (Table I) and ***p*-toluenesulfonate (1g)**. The latter was prepared by reaction of 183 mg (0.65 mmol) of **1f** and 200 mg of *p*-toluenesulfonyl chloride in 10 ml of dry pyridine with stirring overnight at 20°. Extraction of the neutral fraction with ether and three crystallizations from petroleum ether yielded 150 mg (53%) of prisms of **1g**: mp 109–109.5°; ir bands at 7.3, 8.4, and 8.5 μ.

*Anal.* Calcd for $C_{26}H_{40}O_3S$: C, 72.19; H, 9.32. Found: C, 72.47; H, 9.54.

For conversion into the *n*-butyl thio ether, 110 mg (0.25 mmol) of **1g** was refluxed overnight with a solution of 0.3 ml of *n*-butyl mercaptan in 20 ml of *t*-butyl alcohol containing 0.05 g of dissolved potassium. After extraction with chloroform and thorough washing with 1 *N* sodium hydroxide, the resulting mixture was separated by chromatography on basic alumina into olefin **3** and the desired thio ether, $R_f$ 0.42 (1:0). The latter substance (40 mg, 53% yield) was desulfurized with 1 g of W-2 Raney nickel in ethanol (overnight reflux). The resulting hydrocarbon crystallized from methanol when seeded with fichtelite and had essentially identical ir and nmr spectra. Recrystallization furnished 5 mg (17%) of fichtelite, mp 35–40° (mmp 35–45°), which by glpc analysis was 90% pure.

**18-Norabietan-19-al (1h) and 19-Norabietan-18-al (1i).**—To a stirred solution containing 0.60 g (2.14 mmol) of alcohol **1f** in 20 ml of acetone cooled to 0° was added 0.60 ml of Jones reagent[21] at such a rate that the solution remained orange. After 5 min, 5 ml of methanol was added to consume excess reagent. The mixture was then concentrated under reduced pressure and the neutral fraction isolated by extraction with ether and chromatography on 12 g of silica gel. Elution with benzene–petroleum ether (1:3) furnished 270 mg (45%) of **1h** as a colorless oil, $R_f$ 0.65 (6:1), with ir bands at 3.7 and 5.8 μ. The nmr spectrum (Table I) indicated that it was substantially free of the C-4 epimeric aldehyde **1i** (see below). A sample purified by short-path distillation had bp (bath temperature) 150–160° (0.05 mm).

*Anal.* Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.26; H, 11.48.

For epimerization to **1i**, 0.25 g (0.87 mmol) of **1h** was heated for 1 hr at 60° with 1 ml of 2 *N* hydrochloric acid in 10 ml of diglyme under nitrogen. After recovery by extraction with

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(24) Initially, the 131° melting point was found for preparations of the dinitro derivative of **2b** contaminated with **2a**. Recently, this melting point has been confirmed for preparations derived from pure **2b** (private communication from Professor J. W. Huffman, to whom we are most grateful for bringing this fact to our attention).

(25) Melting points were determined in open capillaries with a Hershberg melting point apparatus calibrated against standard substances. Thin layer chromatography (tlc) was performed on microscope slides covered with silica gel G (Merck). $R_f$ values were determined with cyclohexane–ethyl acetate (proportions in parenthesis). Gas–liquid partition chromatography (glpc) was conducted at 200° on a 6-ft 9% SE-30/1% EGip column, to which retention values relative to methyl pimarate ($r_{\mathrm{Pim}}$ = 1.00) are referred. [*Cf.* F. H. M. Nestler and D. F. Zinkel, *Anal. Chem.*, **39**, 1118 (1967). We are deeply grateful to Dr. Zinkel for most of the glpc data recorded herein.] Except where noted otherwise, D-line rotations were measured in ethanol (1–2% solution) with a Perkin-Elmer Model 141 polarimeter. ORD data were obtained in ethanol on a Cary Model 60 recording spectropolarimeter with a 1.0-cm cell. Infrared spectra were recorded in carbon tetrachloride solution on a Perkin-Elmer Model 137 Infracord. Nmr spectra were determined in carbon tetrachloride solution on a Varian A-60 or a HA-100 spectrometer with tetramethylsilane as internal reference. Petroleum ether refers to the fraction with bp 35–45°, Analyses were performed by the Weiler and Strauss Microanalytical Laboratory, Oxford, England.

(26) E. E. Fleck and S. Palkin, *J. Amer. Chem. Soc.*, **60**, 921 (1938).

(27) We thank Professor Paul W. Gilles and Dr. Gordon Lewis of this department for this determination.

ether and repeated washing with water (to remove the diglyme), the product (0.20 g, 80%) had essentially the same tlc behavior as **1h**, but the nmr spectrum (Table I) revealed the absence of the aldehyde and C-10 methyl resonances of **1h** and their replacement by those of **1i**. The sample purified by short-path distillation had bp 150–160° (0.05 mm).

*Anal.* Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.39; H, 11.54.

As an alternative route to **1i**, a solution of 1.00 g (3.8 mmol) of crude **3** in 15 ml of chloroform was added to 1.0 g (5.8 mmol) of *m*-chloroperbenzoic acid at 20°. Tlc indicated that the olefin had reacted completely in less than 10 min. The solution was washed with 1% sodium hydroxide, dried, and evaporated to yield 1.05 g (99%) of epoxide, $R_f$ 0.30. For rearrangement to the aldehyde, 0.96 g of the crude epoxide in 20 ml of benzene was treated with 5 drops of boron trifluoride etherate, whereupon the solution turned golden red. After hydrolysis the mixture was extracted and the product was chromatographed on 20 g of silica gel. Elution with petroleum ether–benzene (4:1) gave nonconjugated olefinic material, $R_f$ 0.80 (6:1). Further elution with a 1:1 mixture of the same solvents afforded 0.39 g (41%) of a mixture **1h** and **1i**, present in a 1:1 ratio, as determined by the nmr spectrum. Acid isomerization converted the mixture into **1i** as above.

**19-Norabietane (1b). A. By Wolff–Kishner Reduction.**—A solution of 130 mg (0.47 mmol) of **1i**, 1 ml of anhydrous hydrazine, and 1 g of potassium hydroxide in 15 ml of diethylene glycol was heated with stirring at 140–160° for 2 hr under nitrogen and then at 210° for 4 hr. After recovery of the product by dilution of the mixture with water and extraction with ether, it was chromatographed on 10 g of acidic alumina, giving in the petroleum ether fractions 75 mg (60%) of hydrocarbon **1b** as an oil: $n^{25}\mathrm{D}$ 1.5005; $[\alpha]\mathrm{D}$ +5°; $R_f$ 0.75 (1:0); and glpc $r_{\mathrm{Pim}}$ 0.40. The nmr spectrum (Table I) indicated the absence of fichtelite (**1a**), but about 10% was present according to glpc. The analytical sample was prepared by short-path distillation: bp (bath temperature) 145–150° (0.5 mm).

*Anal.* Calcd for $C_{19}H_{34}$: C, 86.94; H, 13.06. Found: C, 86.72; H, 13.01.

**B.** *Via* **19-Norabietan-18-ol (1j)**.—Reduction of 276 mg (1.0 mmol) of **1i** with 0.1 g of lithium aluminum hydride in ether afforded, after elution with benzene–ether (19:1) from 5 g of silica gel, 175 mg (63%) of **1j** as a viscous oil: $R_f$ 0.25 (6:1); ir bands at 2.8 and 3.0 μ. Like **1f**, this product was characterized by its nmr spectrum (Table I) and ***p*-toluenesulfonate (1k)** which, however, could not be obtained crystalline. Tosylation of the entire alcohol product by the procedure applied to **1f** furnished 140 mg (51%) of oily **1k**, of which 50 mg was purified for analysis by chromatography on 5 g of silica gel. Tosylate ir bands were present at 7.3, 8.4, and 8.5 μ.

*Anal.* Calcd for $C_{26}H_{40}O_3S$: C, 72.19; H, 9.32. Found: C, 72.55; H, 9.62.

The other portion (90 mg) of **1k** was allowed to react with 0.3 g of potassium *n*-butyl mercaptide in 10 ml of *t*-butyl alcohol (overnight reflux). Chromatography of the product on 5 g of acidic alumina furnished 60 mg (97%) of impure thio ether, $R_f$ 0.43 (1:0), by elution with benzene–petroleum ether (1:2). Olefin **3** could not be detected by nmr analysis of the material in earlier fractions. Desulfurization of the thio ether with 1 g of W-2 Raney nickel, followed by elution from 5 g of acidic alumina with petroleum ether, afforded 30 mg of **1b** (55% from the tosylate): $[\alpha]\mathrm{D}$ +3°; $n^{25}\mathrm{D}$ 1.5000; $R_f$ 0.75 (1:0). The ir and nmr spectra were identical with those of **1b** obtained by route A above. Glpc analysis ($r_{\mathrm{Pim}}$ 0.40) indicated a comparable purity.

**Abietane (1m)**.—Reduction of 0.64 g (2.0 mmol) of the methyl ester (mp 45–46°) of acid **1c**[12] with 0.3 g of lithium aluminum hydride in 20 ml of tetrahydrofuran (overnight stirring at 25°) afforded 0.55 g (94%) of **abietan-18-ol (1n)**, which, after crystallization from methanol, had mp 32–35° (lit.[3c] mp 33–34°). For oxidation to aldehyde **1p**, 0.50 g (1.7 mmol) of **1n** in 25 ml of a stirred solution in acetone cooled to 0° was treated dropwise during 3 min with 0.8 ml of Jones reagent.[21] After 5 min, 2 ml of methanol was added and the mixture was diluted with water and extracted with ether. From the washed and dried ether extracts there was obtained 0.45 g (90%) of oily **abietan-18-al (1p)** having the expected ir absorption at 3.7 and 5.8 μ.[3c] The **2,4-dinitrophenylhydrazone** crystallized from ethanol and then carbon tetrachloride in fine yellow spores, mp 172–173°.

*Anal.* Calcd for $C_{26}H_{38}N_4O_4$: C, 66.36; H, 8.14; N, 11.90. Found: C, 66.32; H, 7.90; N, 12.18.

The **semicarbazone** crystallized from chloroform–ethyl acetate–ethanol as fine needles, mp 245–247°.

*Anal.* Calcd for $C_{21}H_{37}N_3O$: C, 72.58; H, 10.73; N, 12.09. Found: C, 72.69; H, 10.71; N, 11.93.

For conversion into **1m**, 0.35 g (1.0 mmol) of the semicarbazone was mixed with 2.0 g of powdered potassium hydroxide and the mixture was heated to 225–250° for 5 min, when decomposition appeared to be complete. The cooled residue was taken up in water and extracted with petroleum ether to yield 0.18 g of a nearly colorless product, mp 33–35°. After passage through 10 g of acidic alumina with petroleum ether, this afforded 85 mg (31%) of **1m**, mp 34–36°, as translucent plates from ether–ethanol. Recrystallization furnished 65 mg (23%) of pure **abietane (1m)**: mp 38–38.5°; $[\alpha]\mathrm{D}$ ($CCl_4$) −8.5° {lit.[3c] mp 37–38°; $[\alpha]\mathrm{D}$ (*n*-hexane) −5°}; $n^{20}\mathrm{D}$ 1.5042 (supercooled melt); ORD (*c*, 0.25 in hexane) $[\Phi]_{400}$ −35°, $[\Phi]_{250}$ −85°, $[\Phi]_{210}$ −170° (lit.[3c] "plain negative curve"); glpc $r_{\mathrm{Pim}}$ 0.51.

*Anal.* Calcd for $C_{20}H_{36}$: C, 86.88; H, 13.12. Found: C, 86.76; H, 13.21.

**Experiments in the Ring-C Aromatic Series. A. 18-Nor-8,11,13-abietatrien-19-ol (2f) and 19-Nor-8,11,13-abietatrien-18-ol (2j).**—Since work in this series served primarily to develop suitable reaction conditions for the synthesis of **1a** and **1b**, various intermediates were characterized for the most part simply by spectral means. Hydroboration of olefin **4**[15] by the procedure used to obtain **1f** afforded **2f** in comparable yield as a viscous oil. The **3,5-dinitrobenzoate** of **2f**, prepared by reaction with freshly distilled 3,5-dinitrobenzoyl chloride in pyridine at room temperature for 1 hr, crystallized from methanol in faintly yellow clusters: mp 107–109°; C-10 methyl signal at $\tau$ 8.82.

*Anal.* Calcd for $C_{26}H_{30}N_2O_6$: C, 66.93; H, 6.48; N, 6.00. Found: C, 66.58; H, 6.29; N, 6.12.

Oxidation of **2f** to **2h** was conducted with Jones reagent[21] as in the preparation of **1h**. Acid isomerization of **2h** furnished **2i**, which formed a deep yellow **2,4-dinitrophenylhydrazone** that crystallized from ethanol in fine needle clusters, mp 152–154°.

*Anal.* Calcd for $C_{25}H_{30}N_4O_4$: C, 66.65; H, 6.71; N, 12.44. Found: C, 66.78; H, 6.60; N, 12.27.

Reduction of **2i** with lithium aluminum hydride gave **2j** as an oil whose **3,5-dinitrobenzoate**, prepared as above, crystallized from methanol in fine pale yellow needles: mp 126–128°; C-10 methyl signal at $\tau$ 8.76; mmp 79–85° with the 3,5-dinitrobenzoate of **2f**.

*Anal.* Calcd for $C_{26}H_{30}N_2O_6$: C, 66.93; H, 6.48; N, 6.00. Found: C, 66.75; H, 6.77; N, 5.84.

Hydroxylation of **4** with osmium tetroxide in the manner described by Huffman and Stockel[16] gave a glycol, mp 119–120° (lit.[16] mp 101–102°), which was rearranged with 98% formic acid as described by these authors. (In one run the glycol had mp 101–102°, but this result could not be duplicated.) Chromatography of the formic acid product on silica gel afforded roughly equal amounts of an unsaturated hydrocarbon fraction by elution with petroleum ether–benzene (4:1) and an aldehyde-containing fraction by elution with benzene–petroleum ether (1:1). The latter comprised *ca.* equal amounts of **2h** and **2i** (by nmr analysis), contaminated with a small amount of nonaldehydic material (ir absorption at 5.75 μ). This sequence was not applied to **3**.

**B. 12,14-Dinitro Derivatives of 18-Nor-8,11,13-abietatriene (2a) and 19-Nor-8,11,13-abietatriene (2b).**—Oily hydrocarbon **2a** ($r_{\mathrm{Pim}}$ 0.42[28]), prepared from **4** by either of the two methods by which **1a** was obtained from **3**, was nitrated by the procedure of Perold and Jeger.[19b] After purification by chromatography on neutral alumina and elution with benzene–petroleum ether (1:1), the nitration product crystallized from methanol in light yellow needles: mp 176–177.5°; $R_f$ 0.84 (0:1); nmr signal at $\tau$ 2.40 (C-11 aromatic H), 8.64 (d, $J$ = 7 Hz, isopropyl), 8.75 (C-10 methyl), and 8.96 (d, $J$ = 7 Hz, C-4 methyl).

*Anal.* Calcd for $C_{19}H_{26}N_2O_4$: C, 65.88; H, 7.56; N, 8.09. Found: C, 65.51, H, 7.60; N, 8.09.

Hydrocarbon **2b** ($r_{\mathrm{Pim}}$ 0.48[29]), also an oil, was prepared by the thio ether route used to obtain **1b** and was nitrated as above. Chromatography gave a light yellow solid, $R_f$ 0.84 (0:1), which,

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[28] Infrared partly similar to Figure 4, ref 19b.

[29] Infrared as in Figure 3, ref 19b.

after two crystallizations from methanol, had mp 151–153° (other preparations,[24] mp 130–131°); nmr signals at $\tau$ 2.52 (C-11 aromatic H), 8.64 (d, $J$ = 7 Hz, isopropyl), 8.82 (C-10 methyl), and 9.02 (d, $J$ = 5 Hz, C-4 methyl).

*Anal.* Calcd for $C_{19}H_{26}N_2O_4$: C, 65.88; H, 7.56; N, 8.09. Found: C, 66.13; H, 7.81; N, 8.05.

**Registry No.**—**1a**, 2221-95-6; **1b**, 19402-16-5; **1f**, 1451-69-0; **1g**, 3749-83-5; **1h**, 19402-19-8; **1i**, 19407-09-1; **1j**, 19407-10-4; **1k**, 19407-11-5; **1m**, 19407-12-6; **1n**, 15821-26-8; **1p**, 19407-14-8; **1p** (2,4-dinitrophenylhydrazone), 19407-15-9; **1p** (semicarbazone), 19407-16-0; **2a**, 19407-17-1; **2a** (12,14-dinitro derivative), 19407-40-0; **2b**, 19407-18-2; **2b** (12,14-dinitro derivative), 19407-41-1; **2f**, 19407-19-3; **2f** (3,5-dinitrobenzoate), 3858-39-7; **2g**, 19407-21-7; **2h**, 19407-22-8; **2i**, 19407-23-9; **2i** (2,4-dinitrophenylhydrazone), 19407-24-0; **2j**, 19407-25-1; **2j** (3,5-dinitrobenzoate), 1451-73-6; **2k**, 19407-27-3; **2m**, 19407-28-4; **2n**, 19426-88-1; **2p**, 13601-88-2; **3**, 19407-30-8; 4α-methylamino-18-norabietane hydrochloride, 19407-31-9; 4α-dimethylamino-18-norabietane picrate, 19407-32-0.

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# Photochemistry of Isothiochroman-4-one[1–3]

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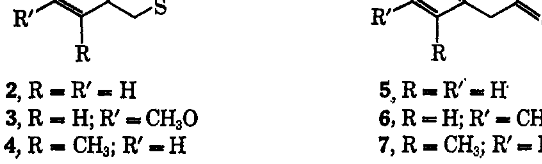
Irradiation of isothiochroman-4-one in cyclohexane (high pressure mercury lamp, Pyrex 7740 filter) produced thiochroman-3-one (21%). Under similar conditions 7-methoxy-, 8-methyl-, 3-methyl-, and 3,3-dimethylisothiochroman-4-one rearranged to 6-methoxy- (40%), 5-methyl- (30%), 2-methyl- (30%), and 2,2-dimethylthiochroman-3-one (37%), respectively. 1,2,3,4-Tetrahydro-1-keto-3-thiaphenanthrene failed to undergo the rearrangement reaction. Irradiation of 5-methyl-2,3-dihydro-2H,6H-thiopyran-3-one under similar conditions resulted in rearrangement to 2-(2-prop-1-enyl)-1-thietan-3-one (28–35%). The pathway for the photochemical conversion of isothiochroman-4-ones into thiochroman-3-ones is discussed.

**Photochemistry.**—The ultraviolet (uv) spectra of β-keto sulfides show evidence for charge transfer in the excited state as well as perturbation of the n,π* state of the carbonyl group.[5–7] Various interpretations of the spectral data have been discussed.[5–8] These effects are not observed in the spectra of β-keto sulfones.[9]

Only two reports have appeared on the photochemistry of β-keto sulfides. Schönberg, Fateen, and Omran[10] obtained radical coupling products (*e.g.*, bidesyl) in the photolysis of desyl aryl sulfides, and La Count and Griffin[11] found that phenacyl benzyl sulfide failed to give the thietanol product from α-hydrogen atom abstraction as did the oxygen analog, phenacyl benzyl ether.

Initial studies confirmed the indication that simple, acyclic β-keto sulfides undergo photochemical reaction involving homolytic cleavage of the α-carbon–sulfur bond. Photolysis of 2-*t*-butylmercaptocyclohexanone (**1**) in cyclohexane for 2 hr produced three products[12] corresponding to 22% of the starting material. Less than 10% **1** remained. The products were identified as di-*t*-butyl disulfide, cyclohexenone, and cyclohexanone and were formed in a ratio of 5:1.4:1. Photolysis in methanol gave the same products in somewhat better yield plus a small amount of 3-*t*-butylmercaptocyclohexanone which was probably formed from Michael addition of *t*-butylmercaptan to cyclohexanone.

In view of the product distribution resulting from β cleavage to radical pairs, it was decided to investigate systems in which the two functionalities were contained in the same ring system. The unsaturated system, isothiochroman-4-one (**2**), was selected. Irradiation of 0.2–0.4% solutions of **2** in cyclohexane or Genetron 113 (1,1,2-trichloro-1,2,2-trifluoroethane) with a Hanovia, Type L, 450-W mercury arc immersion lamp with a Pyrex filter, produced thiochroman-3-one (**5**) in yields of 19–21% and 1-thiaindane in 6% yield. The remainder of the starting material is converted into an amorphous polymeric material which gradually precipitated from the reaction mixture. In a similar fashion 7-methoxyisothiochroman-4-one (**3**) and 8-methylisothiochroman-4-one (**4**) were converted into 6-methoxythiochroman-3-one (**6**) and 5-methylthiochroman-3-one (**7**) in yields of 30 and 40%, respectively. These two examples establish that the sulfur atom in the thiochroman-3-one products is attached to the aryl carbon atom which held the carbonyl function in the starting isothiochroman-4-ones. Photolysis of



**2**, R = R′ = H
**3**, R = H; R′ = $CH_3O$
**4**, R = $CH_3$; R′ = H

**5**, R = R′ = H
**6**, R = H; R′ = $CH_3O$
**7**, R = $CH_3$; R′ = H

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(1) This work was previously reported in communication form.[2]

(2) W. C. Lumma, Jr., and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967).

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(4) To whom inquiries should be sent. Alfred P. Sloan Fellow, 1963–1967.

(5) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71**, 84 (1949).

(6) G. Bergson and A-L. Delin, *Ark. Kemi*, **18**, 489 (1961).

(7) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962).

(8) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p 55.

(9) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71**, 231 (1949).

(10) A. Schönberg, A. K. Fateen, and S. Omran, *ibid.*, **78**, 1224 (1956).

(11) R. B. La Count and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965).

(12) A complex mixture of high boiling material was also isolated, but the constituents were not characterized.