Synthesis of Biological Markers in Fossil Fuels. 1. 17α and 17β Isomers of 30-Norhopane and 30-Normoretane

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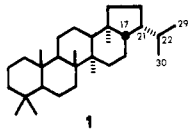
21-Hydroxyhopan-3-one was converted to a mixture of 22,29,30-trinor-17α-hopan-21-one and 30-norhopan-22-one by the following reaction sequence: (1) dehydration with phosphorus oxytrichloride, (2) Wolff–Kishner reduction, and (3) ozonolysis. These two ketones were then utilized to prepare various pentacyclic $C_{29}H_{50}$ hydrocarbons used as biological markers in correlating crude oils and source rocks. 30-Norhopan-22-one was converted to 30-norhopane and 30-normoretane. 22,29,30-Trinor-17α-hopan-21-one was converted to 30-nor-17α-hopane and 30-nor-17α-moretane. The key synthetic feature of these transformations was the efficient application of Barton's tri-*n*-butyltin hydride reduction of *S*-methyl xanthates in order to secure the desired hydrocarbons. The identitiy of synthetic 30-norhopane, 30-normoretane, and 30-nor-17α-hopane with their naturally occurring counterparts was demonstrated by gas chromatography–mass spectrometry. The thermodynamically least stable isomer, 30-nor-17α-moretane, if present at all, was limited to small quantities in fossil fuels.

Degraded triterpenes constitute an important class of biological markers used to solve geochemical problems of crude oils and source rocks. Among these triterpenes, the pentacyclic hydrocarbons derived from hopane (**1**) con-



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stitute one important group of markers that exhibit considerable stereochemical and structural variation. Authentic samples of hopane-derived compounds are a prerequisite for quantitation in correlation applications between crude oils and their source rocks.[1] We report unambiguous syntheses of four isomeric $C_{29}H_{50}$ hydrocarbons:[2] 30-norhopane[3] (**2**), 30-nor-17α-hopane[4] (**3**), 30-normoretane[5] (**4**), and 30-nor-17α-moretane (**5**). This latter compound was of particular interest since the occurrence of 17α-moretanes in petroleum deposits has been suggested[6] but never fully substantiated. 30-Nor-17α-moretane is the compound of least thermodynamic stability of the four hydrocarbons[1e] epimeric at the C-17 and C-21 positions.

Isolation of 22-hydroxyhopan-3-one (**6**) from Dammar resin[7] and subsequent manipulation via a standard sequence[7-9] furnished a mixture of 21-hopene (**7**) and 22-(29)-hopene (**8**) as shown in Scheme I. The separation of these isomers by chromatography on silver nitrate impregnated silica gel was difficult and unnecessary since the ozonolysis[10] of the mixture under carefully controlled conditions gave the readily separable ketones 22,29,30-trinor-17α-hopan-21-one (**9**), 22,29,30-trinorhopan-21-one (**10**), and 30-norhopan-22-one (**11**). The isomerization of **10** to the thermodynamically more stable epimer **9** during ozonolysis was not unexpected,[11] and the base-catalyzed

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(3) For recent reports on the isolation of 30-norhopane from various geological sources, see: (a) Corbet, B.; Albrecht, P. *Storage Ring Phys., Proc. Int. Colloq. Int. CNRS* **1980**, *293*, 221. (b) McEvoy, J.; Eglinton, G.; Maxwell, J. R. *Initial Rep. Deep Sea Drill. Proj.* **1981**, *63*, 763. (c) Kuliev, A. M.; Levshina, A. M.; Shepeleva, T. V. *Dokl. Acad. Nauk Az. SSR* **1980**, *36*, 50. (d) Brassell, S. C.; Comet, P. A.; Eglinton, G.; McEvoy, J.; Maxwell, J. R.; Quirke, J. M. E.; Volkman, J. K. *Initial Rep. Deep Sea Drill. Proj.* **1980**, *50*, 647. (e) Simoneit, B. R. T.; Majurek, M. A. *Ibid.* **1979**, *47* (Part 2), 565. (f) Barnes, P. J.; Brassell, S. C.; Comet, P.; Eglinton, G.; McEvoy, J.; Maxwell, J. R.; Wardroper, A. M. K.; Volkman, J. K. *Ibid.* **1979**, *48*, 965. (g) Simoneit, B. R. T. *Ibid.* **1975** (published 1979), *43*, 643. (i) Kimble, B. J.; Maxwell, J. R.; Philip, R. P.; Eglinton, G.; Albrecht, P.; Ensminger, A.; Arpino, P.; Ourisson, G. *Geochim. Cosmochim. Acta* **1974**, *38*, 1165.

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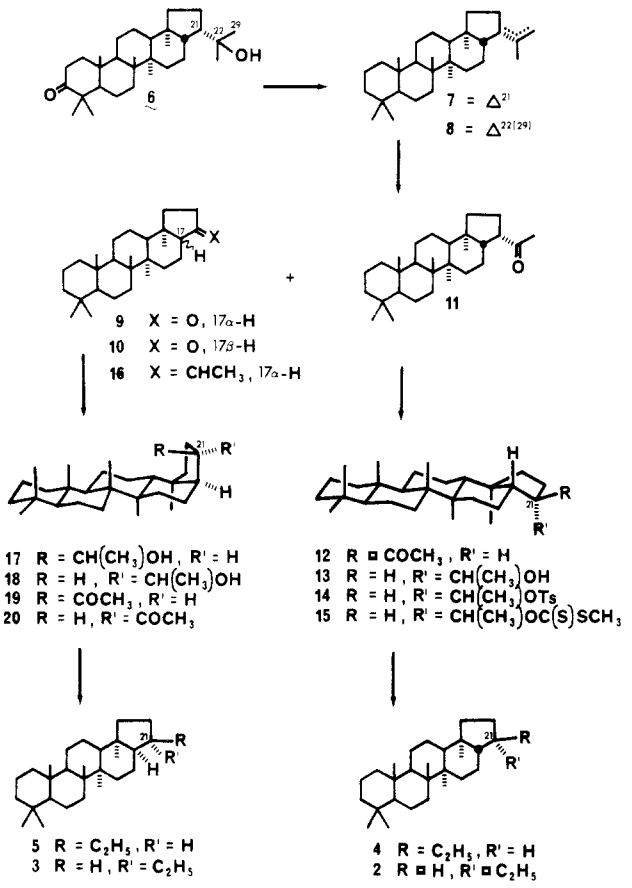
0022-3263/83/1948-4493$01.50/0

Scheme I



isomerization[10] of **10** was routinely performed in order to secure ketone **9**.

In the 17β series, base-catalyzed epimerization of **11** to 30-normoretan-22-one (**12**) and subsequent Wolff–Kishner reduction of **12** secured the expected 30-normoretane[12] (**4**) as shown in Scheme I. In order to obtain the C-21 epimer of **4**, we reduced 30-norhopan-22-one (**11**) with lithium aluminum hydride to 30-norhopan-22-ol (**13**) as a mixture of C-22 diasteromers which were separated by chromatography. Lithium aluminum hydride reduction of the tosylate **14** derived from **13** gave predominantly olefinic products rather than the expected product, 30-norhopane (**2**). The tri-*n*-butyltin hydride reduction[13] of *S*-methyl xanthate derivatives **15** of each of the C-22 diasteromeric alcohols **13** furnished the desired material, 30-norhopane (**2**).

In the 17α series, a Wittig reaction of 22,29,30-trinor-17α-hopan-21-one (**9**) and ethylidenetriphenylphosphorane furnished 30-nor-17α-hop-21-ene[14] (**16**) in 86% yield as a mixture of *E*/*Z* isomers as shown in Scheme I. Hydroboration–oxidation of olefin **16** then provided a mixture of diasteromeric alcohols from which two principal products were separated by chromatography with a solvent system reported by Corbett.[14] The "major" and "minor" products from this hydroboration–oxidation had melting points, R_f values, and ^{1}H NMR spectra in agreement with those of compounds which Corbett[14] assigned as 30-nor-17α-hopan-22-ol (**18**) and 30-nor-17α-moretan-22-ol (**17**), respectively.

The oxidation of the "major" alcohol furnished predominantly the thermodynamically least stable C-21 epimer, 30-nor-17α-moretan-22-one (**19**), and not the product, 30-nor-17α-hopan-22-one (**20**), based on Corbett's structural assignment.[14] Furthermore, conversion of the "major" alcohol to its *S*-methyl xanthate derivative and subsequent reduction with tri-*n*-butyltin hydride[13] gave an 85:15 mixture of 30-nor-17α-moretane (**5**) and 30-nor-17α-hopane (**3**) according to gas chromatography–mass spectral analysis. Consequently, the "major" alcohol from the hydroboration–oxidation reaction was predominantly a C-22 epimer of 30-nor-17α-moretan-22-ol (**17**) contaminated with a small amount of 30-nor-17α-hopan-22-ol (**18**). The reason for the discrepancy between our result obtained using diborane in THF and Corbett's result[14] obtained using $BF_3/LiAlH_4$ in ether was unclear but may be due to a difference in solvent. The "minor" alcohol again furnished 30-nor-17α-moretan-22-one (**19**) on oxidation and a pure sample of 30-nor-17α-moretane (**5**) on reduction of its xanthate derivative. Consequently, the "minor" alcohol was entirely the other C-22 epimer of nor-17α-moretan-22-ol (**17**). Base-catalyzed epimerization of 30-nor-17α-moretan-22-one (**19**) to 30-nor-17α-hopan-22-one (**20**) and subsequent Wolff–Kishner reduction of **20** provided 30-nor-17α-hopane[15] (**3**).

We relied upon a detailed analysis of the ^{13}C NMR data to assess the stereochemical purity of the four isomeric hydrocarbons **2–5**. To distinguish the very similar carbon signals in these hydrocarbons,[16] we successfully employed two recent developments involving distortionless enhancement of polarization transfer[17] (DEPT) and gated spin-echo[18] (GASPE) experiments. These techniques facilitated the rapid identification of all signals shown in Table I and proved particularly useful in our situation where 29 signals appear within a relatively narrow envelope. Several significant differences in the ^{13}C NMR spectra for hydrocarbons **2–5** were noted: (1) the chemical shift of the C-17 resonance appeared at higher field in the 17β series than in the 17α series; (2) the chemical shift of the C-28 methyl group appeared at higher field in the 17β series than in the 17α series. Certain anomalous shifts (C-15, C-19, C-26) in the hydrocarbon **5** and ketone **19**, where the C-17β ethyl and acetyl groups, respectively, were buttressed against the exo face of ring D, may indicate a conformation for **5** and **19** other than the all-chair arrangement in Scheme I.

A study of the gas chromatography–mass spectrometry of the four hydrocarbons **2–5** also confirmed the purity of our materials and provided an opportunity to assess the occurrence of 30-nor-17α-moretane (**5**) in fossil fuels. The question of the presence of 17α-moretanes in fossil fuels was important since they were suggested as potential intermediates in the interconversion of 17α-hopanes and 17α-moretanes in the geosphere (see Figure 5 in ref 1e). We first confirmed previous reports[19] that the stereochemistry at C-17 and C-21 in 30-norhopane, 30-normor-

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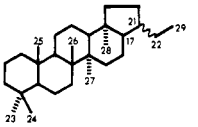
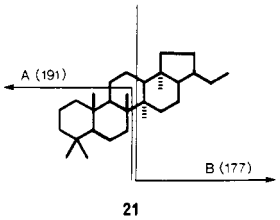
Table I. ^{13}C NMR Data



carbon	shift, ppm						
	2	3	4	5	6	9	19
1	40.36	40.34	40.36	40.27	39.52	40.30	40.21
2	18.72[c]	18.72[c]	18.72[c]	18.52[c]	21.86[c]	18.61[c]	18.42[c]
3	42.14	42.14	42.14	42.11	218.12	42.05	42.05
4	33.32[d]	33.28	33.28	33.29	47.35	33.24	33.27
5	56.15	56.33	56.15	56.54	54.83	56.25	56.50
6	18.72[c]	18.72[c]	18.75[c]	18.75[c]	19.74[c]	18.67[c]	18.70[c]
7	33.32	33.12	33.35	32.93	34.20	32.96	32.87
8	42.39	42.09	42.37	42.36	41.89	41.93	40.30
9	50.46	50.96	50.52	51.13	51.05	50.77	50.96
10	37.44	37.48	37.45	37.51	36.81	37.43	37.46
11	20.95[b]	21.63[b]	21.22[b]	21.53[b]	21.53[b]	21.30[b]	21.33[b]
12	23.99[b]	23.50[b]	23.92[b]	23.99[b]	24.08[b]	23.50[b]	24.12[b]
13	49.27	42.42	48.52	42.68	49.58	38.13	42.42
14	41.96	41.65	41.96	40.70	41.62	40.86[c]	40.70
15	28.68[a]	28.73[a]	27.87[a]	32.44[a]	?	26.87[a]	32.26
16	26.22	25.74	27.62	24.22	34.69	17.50	24.27
17	54.24	52.70	56.74	48.75	53.91	57.44	49.30
18	44.22	44.06	44.52	44.39	44.04	41.56[c]	44.90
19	41.83	41.08	39.75	43.81	41.26	34.58[a]	43.06
20	33.32[a,d]	28.52[a]	32.76[a]	29.88[a]	32.57	35.62	22.13
21	42.10	39.05	41.77	42.68	49.96	221.36	56.44
22	20.52	20.20	20.98	20.22	73.88		210.71
23	33.42	33.39	33.42	33.42	30.88	33.36	33.39
24	21.61	21.58	21.61	21.63	21.12	21.51	21.58
25	16.24	16.13	16.75[c]	16.43	16.20	16.16	16.34
26	16.74	16.31	16.72[c]	21.08	16.45	15.27	21.27
27	15.85	15.91	15.87	15.97	15.71	15.97	15.91
28	16.79	24.19	15.22	26.42	16.88	24.39	25.77
29	13.45	12.79	12.81	13.42	25.36[a]		30.36
30					25.56[a]		

[a-c] Signals may be interchanged. [d] The C-4 quaternary and C-20 CH_2 carbons displayed identical chemical shifts. The C-20 CH_2 was clearly identified in a DEPT experiment,[17] and the C-4 quaternary carbon was detected in a GASPE experiment.[18]

etane, and 30-nor-17α-hopane were distinguished by the ratio of fragments B/A detected at m/e 177 and 191, respectively, as shown in structure **21**. Namely, under 70-eV



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GC/MS conditions, the m/e 177/191 ratios were 1.98 for 30-norhopane (**2**), 1.23 for 30-normoretane (**4**), and 0.42 for 30-nor-17α-hopane (**3**). With the synthetic hydrocarbon **5** in hand, we then established that **5** coeluted with 30-normoretane (**4**) under standard gas chromatographic conditions (60-m DB-1 and DB-5 fused silica capillary columns, J and W Scientific; 100-m Dexsil 400 steel capillary; He or H_2 carrier gas). However, the B/A ratio in the mass spectrum of 30-nor-17α-moretane (0.36) was sufficiently different from that of 30-normoretane (1.2) that any large contribution from 30-nor-17α-moretane would be detectable. For example, a peak composed of 20% 30-nor-17α-moretane (**5**) and 80% 30-normoretane (**4**) would have an m/e 177/191 ratio of approximately 1.0. In tests of numerous rock extracts and crude oils ranging from immature to postmature, the GCMS peaks with retention times corresponding to 30-normoretane/30-nor-17α-moretane had an m/e 177/191 ratio greater than 1. Within the limits of the experimental accuracy of such a measurement, it was clear that 30-nor-17α-moretane was, at most, a minor constituent of that peak.

Experimental Section

Infrared spectra were determined on a Beckman Microlab 600 spectrometer. The abbreviation TF denotes thin film. NMR spectra were determined on a JEOL 270-MHz or a Bruker WH90FT NMR spectrometer. Mass spectra were determined on either a Varian MAT CH5, a Du Pont CEC 21-10B, or a Kratos MS-50 mass spectrometer. Gas chromatography–mass spectroscopy of hydrocarbons **2–5** was performed on a Finnigan 4000 quadrupole system with 60-m DB-1CB or DB-5CB fused silica capillary GC columns from J and W Scientific. The 60-m DB-1CB column was used in a Hewlett-Packard 5880A gas chromatograph for analysis of the hydrocarbons. Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

22,29,30-Trinor-17α-hopan-21-one (9), 22,29,30-Trinorhopan-21-one (10), and 30-Norhopan-22-one (11). To 3.22 g (7.8 mmol) of a mixture[20] of 21-hopene (**7**) and 22(29)-hopene (**8**) [prepared[7b,9a] from 22-hydroxyhopan-3-one (**6**)] in 15 mL of methanol and 500 mL of dichloromethane at −78 °C were introduced a stream of ozone until a faint blue color persisted and then a stream of oxygen until the blue color discharged. An excess of dimethyl sulfide was introduced, and the solution was maintained at −78 °C for 2 h. The solution was warmed to 25 °C, washed with saturated aqueous sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The crude product was

(20) For characterization of the individual isomers, see ref 8a,b and: Ageta, H.; Iwata, K.; Otake, Y. *Chem. Pharm. Bull.* **1963**, *11*, 407.

chromatographed on Merck silica gel F254 with dichloromethane (or 1:10 ethyl acetate–hexane) as an eluent to afford (in the order in which they eluted from the column) 850 mg (26%) of 30-norhopan-22-one [**11**: mp 208–210 °C (lit. mp 218 °C,[21] 222–224 °C[22]); ^{1}H NMR ($CDCl_3$) δ 0.58, 0.79, 0.81, 0.85, 0.93, 0.96 (6 s, 18, quaternary CH_3), 2.11 (s, 3, $COCH_3$)], 470 mg (16%) of 22,29,30-trinor-17α-hopan-21-one (**9**), and, finally, 1.06 g (35%) of 22,29,30-trisnorhopan-21-one (**10**): mp 179–185 °C (lit. mp 180–185 °C,[11] 184–186 °C[23], 175–180 °C[10a]); ^{1}H NMR ($CDCl_3$) δ 0.71, 0.80, 0.83, 0.86, 0.97, and 0.98 (6 s, 18, quaternary CH_3).

Isomerization of 22,29,30-Trinorhopan-21-one (10) to 22,29,30-Trinor-17α-hopan-21-one (9). A solution of 20 mg of 22,29,30-trinorhopan-21-one (**10**) in 0.3 M sodium ethoxide in ethanol was stirred for 12 h and concentrated. The product was diluted with ether, washed with water, and dried over magnesium sulfate to afford 20 mg (100%) of 22,29,30-trinor-17α-hopan-21-one (**9**): mp 219–224 °C (lit. mp 233–240 °C,[11] 244–246 °C,[23] 239–241 °C,[12] 238–240 °C[10a]); IR (KBr) 1727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78, 0.80, 0.84, 1.02, and 1.15 (6 s, signal at 0.84 consists of two superimposed s, 18, quaternary CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 384 (M^+, 29), 369 (10), 191 (100).

Isomerization of 30-Norhopan-22-one (11) to 30-Normoretan-22-one (12). The procedure described for the isomerization of **10** was repeated by using 20 mg of 30-norhopan-22-one (**11**) to afford 20 mg (100%) of 30-normoretan-22-one (**12**): mp 230–232 °C (lit. mp 230–231.5 °C,[21] 232–233 °C[22]); ^{1}H NMR ($CDCl_3$) δ 0.69, 0.79, 0.81, 0.84, 0.95, and 0.96 (6 s, 18 quaternary CH_3), 2.15 (s, 3, $COCH_3$).

30-Normoretane (4). A Wolff–Kishner reduction[9a] was repeated by using 201 mg (0.49 mmol) of 30-normoretan-22-one (**12**) to afford, after chromatography on a Merck silica gel F254 plate in 1:20 ethyl acetate–hexane, 140 mg (72%) of 30-normoretane (**4**): mp 184.5–185.5 °C (lit.[12] mp 171–173 °C); ^{1}H NMR ($CDCl_3$) δ 0.63, 0.79, 0.81, 0.85, 0.94, and 0.96 (6 s, 18, quaternary CH_3); GC/MS (70 eV), *m/e* (relative intensity) 398 (7, M^+), 383 (9), 369 (1), 191 (81), 177 (100). Anal. ($C_{29}H_{50}$) C, H. The purity of this product by capillary GC analysis was 99.9%.

30-Norhopan-22-ol (13). To 11.2 mg (0.294 mmol, 4.8 equiv) of lithium aluminum hydride in 0.5 mL of anhydrous ether was added 100 mg (0.243 mmol) of 30-norhopan-22-one (**11**) in 4 mL of THF. The reaction mixture was stirred for 1.5 h and quenched with ice. The product was isolated in the usual fashion and chromatographed on Merck silica gel F254 in 1:15 ethyl acetate–dichloromethane to give the two alcohols **13a** and **13b** which were epimeric at C-22.

One band (R_f 0.20) afforded **13a**: 54 mg (53%); mp 203–205 °C; IR (KBr) 3435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.72, 0.79, 0.81, 0.84, and 0.96 (6 s, signal at 0.96 consists of two superimposed s, 18, quaternary CH_3), 1.10 (d, J = 5.9 Hz, 3, $CH(OH)CH_3$), 3.7–3.89 (m, 1, $CH(OH)CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 414 (35), 369 (30), 191 (100). Anal. ($C_{29}H_{50}O$) C, H.

Another band (R_f 0.09) afforded **13b**: 35 mg (35%); mp 220–222 °C; IR (KBr) 3416 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.72, 0.79, 0.81, 0.84, 0.94, and 0.96 (6 s, 18 quaternary CH_3), 1.20 (d, J = 5.9 Hz, 3, $CH(OH)CH_3$), 3.67–3.87 (m, 1, $CH(OH)CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 414 (15), 369 (20), 193 (100). Anal. ($C_{29}H_{50}O$) C, H.

***S*-Methyl *O*-30-Norhopan-22-yl Dithiocarbonate (15).** The procedure of Barton[13] was repeated by using 50 mg (0.121 mmol) of 30-norhopan-22-ol (**13a**), 0.15 mL of 1.18 M (0.181 mmol, 2.5 equiv) *n*-butyllithium in hexane, 0.044 mL (0.725 mmol, 6 equiv) of carbon disulfide, and 0.045 mL (0.725 mmol, 6 equiv) of methyl iodide to afford, after chromatography on Macherey-Nagel silica gel F254 in hexane, **15a**: 44 mg (71%); mp 197–198 °C; IR (KBr) 1221, 1235 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.73, 0.78, 0.81, 0.84, 0.91, and 0.94 (6 s, 18, quaternary CH_3), 1.24 (d, J = 5.9 Hz, 3, $CH(CH_3)OCS_2CH_3$), 2.55 (s, 3, CS_2CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 504 (1), 397 (100), 107 (25). Anal. ($C_{31}H_{52}OS_2$) C, H.

Repetition of this procedure using 30 mg (0.073 mmol) of 30-norhopan-22-ol (**13b**) furnished 34 mg (94%) of xanthate **15b**: mp 205–206 °C; IR (KBr) 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78, 0.79, 0.81, 0.84, 0.94, and 0.96 (6 s, 18, quaternary CH_3), 1.33 (d, J = 5.9 Hz, 3, $CH(CH_3)OCS_2CH_3$), 2.54 (s, 3, CS_2CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 504 (4), 489 (2), 397 (54), 191 (100). Anal. ($C_{31}H_{52}OS_2$) C, H.

30-Norhopane (2). The procedure of Barton[13] was repeated by using 0.08 mL of tri-*n*-butyltin hydride (0.297 mmol, 5 equiv) and 30 mg (0.060 mmol) of *S*-methyl *O*-30-norhopan-22-yl dithiocarbonate (**15b**) to afford, after chromatography on Macherey-Nagel silica gel F254 in hexane, 43.9 mg of 30-norhopane (**2**) contaminated by tin-containing byproducts. To 450 mg (4.5 mmol) of chromium trioxide in 0.7 mL of pyridine and 5.9 mL of dichloromethane was added the above mixture in 0.7 mL of dichloromethane. The mixture was stirred for 5 h at 25 °C. The product was isolated in the usual fashion to afford, after chromatography on Macherey-Nagel silica gel F254 in hexane, **2**: 11 mg (46%); mp 172–174 °C; ^{1}H NMR ($CDCl_3$) δ 0.69, 0.79, 0.81, 0.84, 0.93, and 0.96 (6 s, 18, quaternary CH_3); GC/MS (70 eV), *m/e* (relative intensity), 398 (9, M^+), 383 (8), 191 (50), 177 (100). Anal. ($C_{29}H_{50}$) C, H. The purity of this product by capillary GC analysis was 100%. This product was identified by GC coinjection, GC/MS, and ^{1}H NMR comparison with authentic 30-norhopane obtained from P. Albrecht.[2c]

30-Nor-17α-hop-21-ene (16). The procedure of Corbett[14] was repeated by using 144 mg (6 mmol, 12 equiv) of sodium hydride, 2.59 g (7 mmol, 14 equiv) of ethyltriphenylphosphonium bromide, and 192.5 mg (0.5 mmol) of recrystallized ketone **9** to afford a crude product that was chromatographed on silver nitrate impregnated Macherey-Nagel silica gel F254 in hexane to afford 170 mg (86%) of 30-nor-17α-hop-21-enes[14] (**16**) as a mixture of *E/Z* isomers.

30-Nor-17α-moretan-22-ol (17). To 646 mg (1.63 mmol) of 30-nor-17α-hop-21-enes (**16**) in 24 mL of anhydrous hexane at 0 °C under a nitrogen atmosphere was added 8.15 mL of 1 M borane (8.15 mmol, 10 equiv) in THF. The solution was stirred for 3.5 h at 25 °C, cooled to 0 °C, and diluted with 6 mL of 3 M sodium hydroxide solution followed by 6 mL of 30% hydrogen peroxide solution. The mixture was stirred for 10 h at 25 °C, diluted with 100 mL of ether, washed successively with water, sodium bisulfite solution, water, and brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on a low-pressure LC by using Woelm silica gel and 1:1 ethyl acetate–hexane.

Fractions 34–39 ("major" alcohol) afforded 413 mg (61%) of an 85:15 mixture of 30-nor-17α-hopan-22-ol (**17**, either the 22*R* or 22*S* epimer) and 30-nor-17α-hopan-22-ol (**18**): R_f 0.74; ^{1}H NMR ($CDCl_3$) δ 0.79, 0.80, 0.84, 0.91, 0.96, and 1.03 (6 s, 18, quaternary CH_3), 1.19 (d, J = 6.6 Hz, 3, $CHCH_3$); ^{13}C NMR ($CDCl_3$) δ 69.8 (C-22). These data are in agreement with the data reported by Corbett[14] for 30-nor-17α-hopan-22-ol (**18**) but are inconsistent with our observation that the pyridinium chlorochromate oxidation of our "major" alcohol gave predominantly 30-nor-17α-moretan-22-one (**19**).

Fractions 40–44 ("minor" alcohol) afforded 136 mg (20%) of 30-nor-17α-moretan-22-ol (**17**, either the 22*R* or the 22*S* epimer): mp 203–204 °C; R_f 0.65; ^{1}H NMR ($CDCl_3$) δ 0.80, 0.85, 0.91, 0.96, and 1.02 (6 s, signal at 0.80 consists of two superimposed s, 18, quaternary CH_3), 1.21 (d, J = 5.9 Hz, 3, $CHCH_3$); ^{13}C NMR ($CDCl_3$) δ 70.9 (C-22). These data are in agreement with the data reported by Corbett[14] for **17**, and this structural assignment was confirmed by pyridinium chlorochromate oxidation of our material to 30-nor-17α-moretan-22-one (**19**) as well as subsequent conversion to 30-nor-17α-moretane (**5**).

30-Nor-17α-moretane (5). The procedure described for the preparation of **2** was repeated by using 55 mg (0.13 mmol) of 30-nor-17α-moretane-22-ol (**17**, "minor" alcohol) to afford a xanthate derivative: 49 mg (74%); mp 181–182.5 °C; IR (KBr) 1219, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79, 0.84, 0.89, 0.98, and 1.01 (6 s, signal at 0.79 consists of two superimposed s, 18, quaternary CH_3), 1.35 (d, J = 5.9 Hz, 3, $CH(CH_3)OCS_2CH_3$), 2.54 (s, 3, CS_2CH_3). The xanthate (63 mg) was reduced with tri-*n*-butyltin hydride and purified by chromium trioxide oxidation of tin-containing byproducts to give **5**: 26 mg (52%); mp 178–179 °C; ^{1}H NMR ($CDCl_3$) δ 0.79, 0.80, 0.84, 0.90, 0.94, and 1.02 (6 s, 18,

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quaternary CH_3); GC/MS (70 eV), *m/e* (relative intensity) 398 (20, M^+), 383 (13), 369 (1), 191 (100), 177 (36). Anal. ($C_{29}H_{50}$) C, H. The purity of this product by capillary GC analysis was 99%.

30-Nor-17α-moretan-22-one (19). To 33 mg (0.153 mmol) of pyridinium chlorochromate in 0.5 mL of dichloromethane was added 42 mg (0.102 mmol) of alcohol 17 in 1.0 mL of dichloromethane. The mixture was stirred for 2.5 h at 25 °C, diluted with ether, and filtered. The filtrate was concentrated and chromatographed on Macherey-Nagel silica gel F254 in 1:3:5 ether–hexane–dichloromethane to afford 30-nor-17α-moretan-22-one (19): 30 mg (72%); mp 190–191 °C; ^1H NMR ($CDCl_3$) δ 0.80, 0.84, 0.88, 1.00, and 1.04 (6 s, signal at 0.80 consists of two superimposed s, 18, quaternary CH_3), 2.13 (s, 3, $COCH_3$). These NMR data are in agreement with literature values.[14]

30-Nor-17α-hopan-22-one (20). The procedure described for the preparation of **9** was repeated with 5.4 mg (0.131 mmol) of ketone **19** to afford, after chromatography on Merck silica gel F254 in 1:10 ethyl acetate–hexane, 4.7 mg (87%) of 30-nor-17α-hopan-22-one (**20**) having ^1H NMR data in accord with literature values.[14]

30-Nor-17α-hopane (3). A Wolff–Kishner reduction was repeated with 30.5 mg (0.74 mmol) of 30-nor-17α-hopan-22-one (**20**) to afford, after chromatography on Merck silica gel F254 in hexane, 30-nor-17α-hopane (**3**): 15.2 mg (52%); mp 173–174.5 °C; ^1H NMR ($CDCl_3$) δ 0.79, 0.82, 0.85, 0.93, 0.96 and 0.99 (6 s, 18, quaternary CH_3); GC/MS (70 eV), *m/e* (relative intensity) 398 (33, M^+), 383 (22), 369 (2), 191 (100), 177 (42). Anal. ($C_{29}H_{50}$) C, H. The purity of this product by capillary GC analysis was 97.9%. This product was identical by GC coinjection, GC/MS, and ^1H NMR comparison with authentic 30-nor-17α-hopane obtained from P. Albrecht.[2b]

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Kinetics of Decarboxylation of the Two Epimers of 5-*tert*-Butyl-1-methyl-2-oxocyclohexanecarboxylic Acid: Lack of Stereoelectronic Control in β-Keto Acid Decarboxylation

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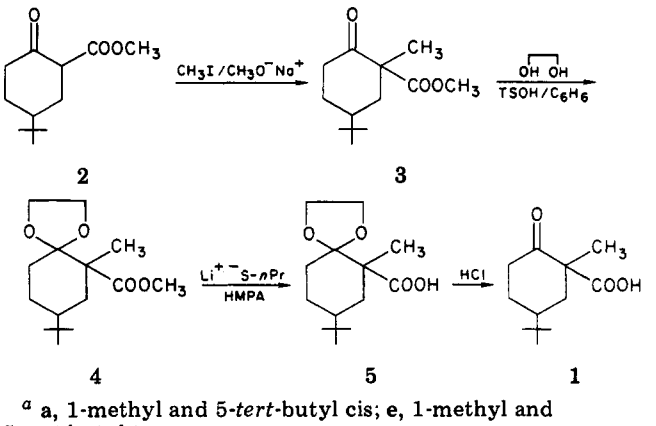
Rates of decarboxylation of the two epimers of 5-*tert*-butyl-1-methyl-2-oxocyclohexanecarboxylic acid have been measured under both acidic and basic conditions at 25 °C. The decomposition of isomer **1e** (methyl and *tert*-butyl trans) is more rapid than that of isomer **1a** (methyl and *tert*-butyl cis) both in acid (about 3-fold) and in base (15- to 20-fold). These results are not in agreement with the principle of stereoelectronic control. Reasons for this discrepancy are discussed.

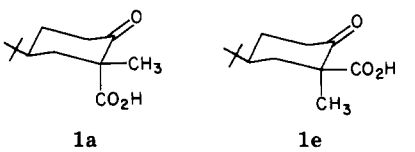
Stereoelectronic control of the enolization of ketones has been the subject of many investigations since the pioneering work of Corey and Sneen.[1] They postulated that, in the absence of large steric effects to the contrary, α axial hydrogens of cyclohexanones will be lost more readily than α equatorial ones since the axial C–H bond is correctly aligned to give continuous overlap with the π orbital of the carbonyl group during enolization. Although this theory is attractive and widely accepted,[2a] actual rate discriminations are often small.[1,3-5] Recently, however, Fraser and Champagne have reported a large selectivity in the base-catalyzed exchange of the protons α to the carbonyl group of a dibenzocycloheptadienone derivative (73:1)[6a] and a twistan-4-one (270:1),[6b] and Spencer[7] has demonstrated the highly selective (>100:1) abstraction of axial α protons from iminium ions of *trans*-decalone derivatives as well as the corresponding ketones.

Scheme I[a]



[a] **a**, 1-methyl and 5-*tert*-butyl cis; **e**, 1-methyl and 5-*tert*-butyl trans.

We wish to report here the relative rates of decarboxylation of the two epimeric 5-*tert*-butyl-1-methyl-2-oxocyclohexanecarboxylic acids **1a** and **1e**, a reaction formally



1a **1e**

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