benzene reacts to produce some trimethyl- and pentamethylbenzenesulfonates. These rearrangements proceed rapidly under conditions where the aromatic system is protonated. In the case of the aromatic systems strong acids are required; the porphyrins, on the other hand, are much stronger bases, requiring only organic acids for protonation. It would appear that sufficiently high temperatures and geologic time could produce the observed migrations. A further example of the relative ease of the loss of peripheral groups from the porphyrins is the production of deuteroporphyrin from protoporphyrin by the loss of two vinyl groups. This reaction is carried out in about 0.5 hr in fused resorcinol at 160–180°. The mechanism has not been established but is generally referred to as a transvinylation reaction, either ionic or free radical. While no direct evidence in favor of any mechanism can be offered, transalkylation *via* an ionic or free-radical mechanism could help to account for the multitude of reaction products observed.

Experimental Section

Asphaltenes were prepared in the standard way by precipitation from the crude petroleum with 10 parts of pentane at room temperature. The precipitated asphaltenes were rewashed with pentane and recovered by filtration or centrifugation. Some samples were further purified by exhaustive Soxhlet extraction. The petroporphyrins were prepared by extraction from the asphaltenes with methanesulfonic acid.[9] The porphyrins were recovered from the methanesulfonic acid by extraction with methylene chloride and purified by chromatography over silica gel with cyclohexane–benzene–ether. Visible absorption spectra were taken on a Beckman DK-1 recording spectrophotometer. Mass spectra were taken on an AEI MS-9 double-focusing mass spectrometer, fitted with a direct sample insertion lock. Source temperatures and ionizing potential were selected to give only parent molecular ions. Typical conditions were 230–250° and 7–9 ev.

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Communications to the Editor

A Novel Biscyclopropylcarbinyl System[1]

Sir:

We wish to report the preparation and some of the chemical behavior of two novel epimeric biscyclopropylcarbinols which are of interest as nonclassical carbonium ion precursors,[2a] as well as in other connections.[2b]

The compounds in question were derived from the recently reported[2c] II-COOH, mp 185° dec, which was in turn obtained from the Simmons–Smith reaction on the methyl ester of dihydrohydrindacenecarboxylic acid[2c] (I). Acid II-COOH reacts readily with $Pb(OAc)_4$ and pyridine in benzene solution[3] even at room temperature to give a *ca.* 60% yield of an acetate[4] II-OAc, mp 92–93°, whose nmr spectrum $(CCl)_4$ shows a singlet at τ 4.32 for the C_4 α-proton, an AB quartet with $J_{AB} = 6$ cps, τ_A 9.50 and τ_B 9.62 for four cyclopropane protons, and an AB quartet with $J_{AB} = 14$ cps, τ_A 7.62 and τ_B 8.22 for the two C_8 protons. Solvolytically, this acetate is one of the most reactive *secondary* esters ever encountered.[2a] Thus, attempted saponification with methanolic KOH gives only partially the saponification product, II–OH, along with considerable solvolysis product, II-OMe. The latter,[4] bp 82–84° (4 mm), is obtained exclusively when the acetate is refluxed in methanol for 10 min. The nmr spectrum (CCl_4) of II-OMe, showing a singlet for the α-proton at τ 6.24, is consistent with the indicated structure.

The high solvolytic reactivity of II-OAc provides an effective route to the parent hydrocarbon and thus direct evidence regarding the relative configurations of the two cyclopropane groups. In 65% aqueous diglyme containing concentrated $NaBH_4$, acetate II-OAc is converted rapidly at 50° to the parent hydrocarbon[4] II-H, bp 92° (4 mm). No alcohol product is observed, so carbonium ion trapping[5] by the BH_4^- is extremely efficient, indicating a relatively stable and long-lived cationic intermediate. Acetate II-OAc is also converted to hydrocarbon II-H, but less smoothly, by hydrogenolysis with PtO_2 catalyst in ethanol. The nmr spectrum (CCl_4) of hydrocarbon II-H shows an AB quartet for the four C_4 and C_8 protons with $J_{AB} = 15$ cps, τ_A 8.01 and τ_B 8.17, and another AB quartet for the four cyclopropane protons with $J_{AB} = 5$ cps, τ_A 9.77 and τ_B 10.05. This spectrum, indicating two kinds of proton on C_4 and C_8, contrasts with that of hydrocarbon VI which has a *trans* relationship of the two cyclopropane methylenes. The two hydrocarbons are also distinguishable and separable by vpc.

The *trans* hydrocarbon VI may be obtained from the dihydrohydrindacene[4] III, mp 90°, which is obtained in 80% yield from Birch reduction of *s*-hydrindacene.[6] In its nmr spectrum (CCl_4), III shows a singlet signal

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[1] Reported in part at the Annual Meeting of the Japanese Chemical Society, Osaka, Japan, April 4, 1965, and the Japanese–American Seminar in Physical Organic Chemistry, Kyoto, Japan, April 6–10, 1965.

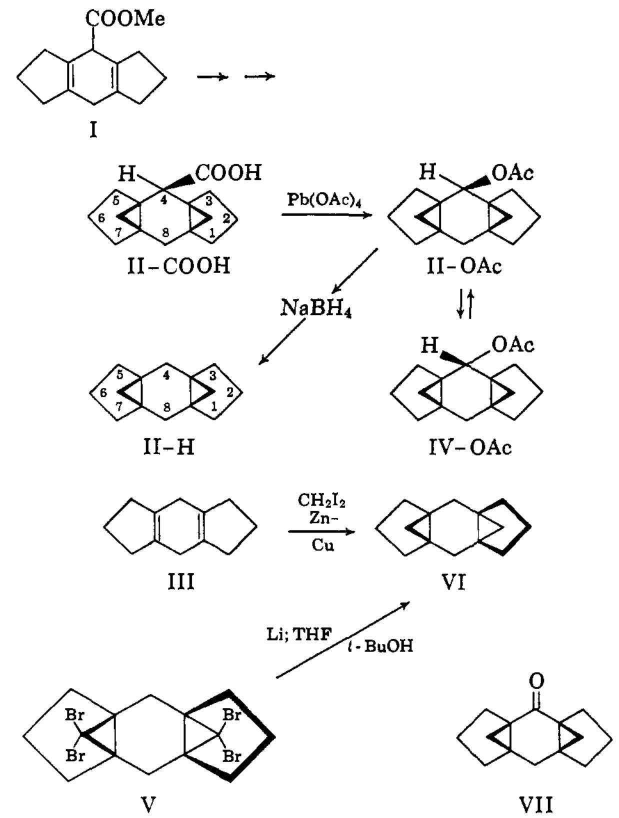
[2] (a) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966); (b) L. Birladeanu and T. Hanafusa, unpublished work; (c) T. Hanafusa, L. Birladeanu, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3510 (1965).

[3] (a) E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); (b) J. K. Kochi, *ibid.*, **87**, 1811, 2500 (1965).

[4] The indicated compounds gave satisfactory carbon and hydrogen analyses.

[5] (a) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) S. Winstein, A. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

[6] R. T. Arnold and E. Rondestvedt, *ibid.*, **67**, 1265 (1945).



at τ 7.51 for four bisallylic protons and no vinyl proton signal. One route from III to VI is by way of the bisdibromocarbene adduct[4] V, mp 260–263°, obtained along with monodibromocarbene adduct,[4] mp 30–32°, from treatment of III with $CHBr_3$ and KOBu-*t*. The *trans* relationship of the cyclopropane groups in V is indicated by a zero dipole moment[7a] as well as by the nmr spectrum (CCl_4) which shows a sharp singlet for four protons at τ 8.33 corresponding to only one variety of C_4 and C_8 proton. Debromination of V with Li and *t*-BuOH in THF leads to the parent *trans* hydrocarbon[4] VI, mp 49–50°, whose nmr spectrum (CCl_4), with a sharp singlet at τ 8.22 for the four equivalent C_4 and C_8 protons,[7b] and an AB quartet with J_{AB} = 5 cps, τ_A 9.59 and τ_B 10.07 for the four cyclopropane protons, is consistent with the *trans* designation.[7b] The parent *trans* hydrocarbon VI (>99.5% *trans*) is also obtained from the Simmons–Smith reaction on the dihydrohydrindacene III. This result is thus in striking contrast with the one observed from the Simmons–Smith reaction on the dihydrohydrindacenecarboxylic ester I, emphasizing the directing effect of the COOMe group.[2c]

On the basis of the available evidence it is thus clear that the compounds designated by II have the *cis* relationship of the cyclopropane groups. The arguments for an all-*cis* configuration of II-COOH with the carboxyl group also *cis* have been given previously.[2c] That acetate II-OAc is also the *cis* epimer is clear from additional evidence. Thus, treatment of II-OAc with $LiAlH_4$ in ether gives rise to the corresponding alcohol[4] II-OH, mp 90–91°, whose nmr spectrum (CCl_4) shows a singlet at τ 5.83 for the α-proton. This alcohol is converted readily by active MnO_2 to the corresponding ketone[4] VII, mp 123–124°, carbonyl stretching frequency 1655 cm^{-1}, whose nmr spectrum (CCl_4) shows an AB quartet with J_{AB} = 6 cps, τ_A 9.16 and τ_B 9.60 for four cyclopropane protons. Reduction of this ketone gives rise to mixtures of alcohol II-OH and its epimer IV-OH, containing *ca.* 50% of the epimer when $LiAlH_4$ is employed in ether and *ca.* 80% of the epimer when 0.25 *M* $NaBH_4$ is used in refluxing *i*-PrOH (22 hr). Twice recrystallized IV-OH,[4] mp 102–104°, shows in its nmr spectrum (CCl_4) a singlet at τ 6.52 for the α-proton. By holding reaction times to a minimum, this alcohol may be acetylated with Ac_2O in pyridine at room temperature to yield the corresponding acetate[4] IV-OAc, mp 58–61°, whose nmr spectrum shows a singlet at τ 5.46 for the α-proton and an AB quartet with J_{AB} = 5 cps, τ_A 9.43 and τ_B 9.93 for the cyclopropane protons.

Attempts to equilibrate the epimeric alcohols II-OH and IV-OH by conventional means, using Al(OPr-*i*)$_3$ in *i*-PrOH, were unsuccessful because of the great tendency toward ionization displayed by these systems. Thus, ether formation competes too well with equilibration. However, it is possible to equilibrate the acetates smoothly in Ac_2O. In this solvent at room temperature, acetate IV-OAc undergoes very clean epimeric equilibration with a half-life of *ca.* 1 hr (k = *ca.* 2×10^{-4} sec^{-1}). At equilibrium the epimeric ratio, II-OAc:IV-OAc, is 98.97:1.03 as analyzed by nmr using a Varian C-1024 time-averaging computer (CAT) on 100 scans of the α-proton region of the spectrum.

That the *cis* epimeric assignment should be given to II-OAc and II-OH and the *trans* assignment to IV-OAc and IV-OH is clear on the basis of two criteria. One is the considerably higher nmr chemical shift for the α-proton in the IV-OH and IV-OAc relative to II-OH and II-OAc due to the shielding effect of the cyclopropane rings *cis* to the α-proton in the IV derivatives.[7b] The other is the greater thermodynamic stability of the II-OAc relative to IV-OAc, models predicting greater opposition to an acetoxy group from the cyclopentano groups in IV-OAc than from the cyclopropano groups in II-OAc. On the basis of the nmr evidence, the II-OMe is also *cis*, the solvolysis of II-OAc being highly stereospecific.[2a] The same kind of stereospecificity is obviously associated with the II-COOH–Pb(OAc)$_4$ reaction, product formation probably occurring here from a carbonium ion.[3]

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Rate and Stereochemistry of Solvolysis of a Biscyclopropylcarbinyl System[1]

Sir:

We have previously discussed[2b] the possible multiplicity of nonclassical structures for ions related to

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[7] (a) W. D. Kumler, private communication. For a related case, see W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Am. Chem. Soc.*, **86**, 3126 (1964); (b) see R. S. Boikess and S. Winstein, *ibid.*, **85**, 343 (1963), for analogous nmr examples.

[1] (a) Research supported in part by the National Science Foundation; (b) reported in part at the Annual Meeting of the Japanese Chemical Society, Osaka, Japan, April 4, 1965, and the Japanese-American Seminar in Physical Organic Chemistry, Kyoto, Japan, April 6–10, 1965.

[2] (a) See P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc.,