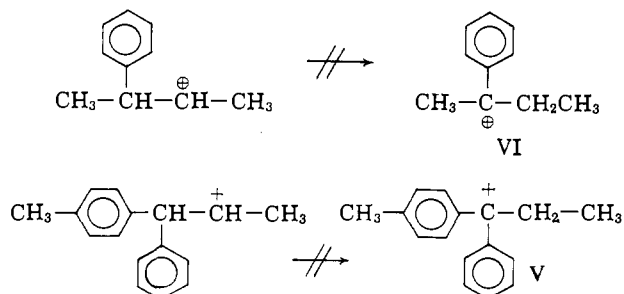


lack of resolution of the methyl band at -120° seems to favor structure III, but a clear choice between III and IV is not possible.

The ionization of *erythro*- and *threo*-3-phenyl-2-butanols at -60° gave the n.m.r. spectrum in Figure 2, showing two methyl doublets at -1.37 and -1.68 p.p.m. These doublets are attributed to the methyls in ions Ia and Ib in an equimolar mixture. The hydrogens on the cyclopropane ring are found between -3.0 and -3.50 p.p.m. This agrees exactly with the -3.44 p.p.m. band for the cyclopropane hydrogens Winstein and Ebersson found in the anthrylethyl-bridged ion.⁶ The ring hydrogens exhibit bands centered at -8.02 p.p.m. (quadruplet) and -9.54 p.p.m. (doublet) and do not resemble the spectra of any other known aryl-carbonium ion. However, this region is similar to the spectra of protonated benzene and toluenes previously observed, which should provide the ideal model for comparison,⁷ and to the -9.60 value of the hydrogen on the 10-position of the anthrylethyl-bridged ion.^{6,8} Drowning the solution of I gave a good yield of monomer alcohols and olefins, demonstrating a polymer ion was not being observed. 1-*p*-Methylphenyl-1-phenyl-2-propanol in our system gave the spectrum shown in Figure 3 (the assignments are shown in structure II). This is obviously not the spectrum of V, as the spectrum in Figure 2 is not that of VI. Both V and VI were expected to be formed *via* 1,2-hydride shifts if the corresponding classical carbonium ions would be more stable in our solvent system than the bridged phenonium ions.



In all spectra the areas were in accord with theory. The results reported here should not be extrapolated to previous stereochemical and kinetic solvolyses studies since in our highly acidic and ionizing solvent a shift from possible equilibrating ions, in more basic solvents, to static bridged ions would be favored.

(6) L. Ebersson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

(7) G. A. Olah, *ibid.*, **87**, 1103 (1965).

(8) Although interpretation of the ring proton in I is not easy (it is an A_2B_2C system further complicated, being a mixture of Ia and Ib with nonidentical *ortho* protons), the experimentally observed spectra is consistent with one of the many allowed patterns.

Acknowledgment. We are grateful to Professor H. C. Brown for samples of *erythro*- and *threo*-3-phenyl-2-butanols and to Dr. C. J. Collins for a sample of 3-phenyl-3-*p*-tolyl-2-butanol.

G. A. Olah, C. U. Pittman, Jr.

Contribution from the Eastern Research Laboratories
Dow Chemical Company, Wayland, Massachusetts

Received April 22, 1965

Introduction of an Angular Methyl Group by Decarboxylative Cyclopropane Ring Opening¹

Sir:

We wish to report a novel decarboxylative cyclopropane ring opening with formation of an angular methyl group which we encountered while studying the carboxylic acid III-COOH. This acid, needed in the course of another investigation,² was obtained from Birch reduction of 4-hydrindacenecarboxylic acid³ (I), m.p. $232-233^\circ$, to II-COOH,⁴ m.p. $156-158^\circ$, conversion of II-COOH to its methyl ester⁴ II-COOME, m.p. $40-41^\circ$, with diazomethane, and then the Simmons-Smith reaction⁵ on II-COOME. Saponification of the crude product and recrystallization led to pure III-COOH,⁴ m.p. 185° dec., in 45% over-all yield from II-COOME. Although a careful search for another bis adduct has not yet been made, it is clear that the Simmons-Smith reaction with II-COOME is at least moderately stereospecific.

In its n.m.r. spectrum (CCl_4) III-COOH showed a singlet at τ 7.13 for the α -proton, a singlet at τ 9.71 for 4 cyclopropane protons, and an AB quartet (partly hidden under the remaining methylene signals) for the C-8 methylene protons, with $J_{AB} = 14$ c.p.s., τ_A 7.69, and τ_B 8.29. As regards stereochemistry, the acid III-COOH is judged to be the all-*cis* form. The most direct evidence for the *cis* relationship between the two cyclopropane methylenes is the conversion of the acid to the parent *cis* hydrocarbon III-H by methods not involving opening of the cyclopropane rings.² That the carboxyl group in III-COOH is *cis* to the cyclopropane methylene group is indicated by physical and chemical considerations. The singlet signal for the cyclopropane protons in III-COOH, due to essentially identical chemical shifts for the "inside" and "outside" protons, is ascribed to the presence of the *cis*-carboxyl group which has a differential effect on the "inside" relative to the "outside" protons. By contrast, the cyclopropane methylene signal appears as an AB quartet in the *cis* hydrocarbon III-H and other derivatives, as well as the *trans* hydrocarbon.² The tendency toward stereospecificity in the Simmons-Smith reaction on II-COOME also speaks for the all-*cis* configuration for III-COOH since the preferred *cis* relationship between the cyclopropane rings may be ascribed to a directing effect of the COOME group akin to the *cis*-directing

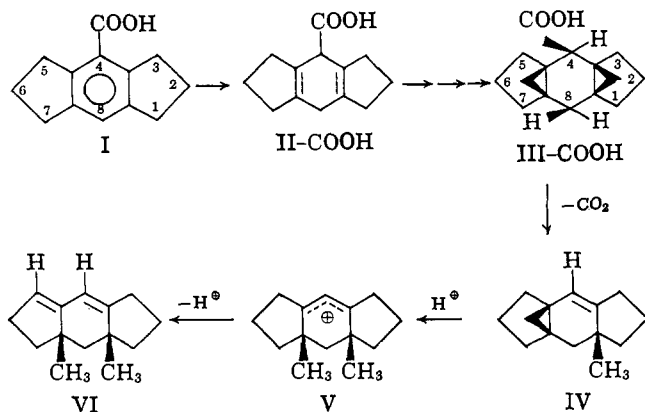
(1) Reported in outline at the Annual Meeting of the Japanese Chemical Society, Osaka, Japan, April 4, 1965.

(2) L. Birladeanu and T. Hanafusa, unpublished work.

(3) R. T. Arnold and E. Rondstedt, *J. Am. Chem. Soc.*, **67**, 1265 (1945).

(4) The indicated compounds gave satisfactory carbon and hydrogen analyses.

(5) (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961); P. Radlick and S. Winstein, *ibid.*, **86**, 1866 (1964); W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).



effect^{6b} of OH and OCH₃. It is pertinent that, without the COOMe group, the parent dihydrohydrindacene II-H gives a *trans* orientation of the two cyclopropane rings in the Simmons-Smith reaction.²

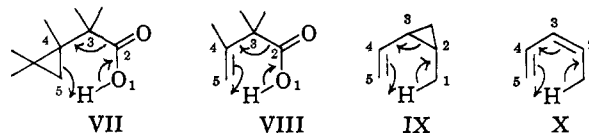
Above its melting point, the acid III-COOH was observed to lose CO₂ readily. In a sealed evacuated ampoule for 4.5 hr. at 204–209°, III-COOH was converted quantitatively to a 97:3 mixture of a monoolefin IV and a diolefin, probably VI. The diolefin was obviously a secondary product from a carboxylic acid catalyzed reaction of the monoolefin IV. Thus the identical treatment of III-COOH containing *ca.* 20% of aromatic acid I produced a 47:44:9 mixture (v.p.c.) of IV, VI, and an unidentified peak, respectively. In 1.7 hr., reaction of the contaminated III-COOH was complete, the product mixture being 75:21:4. However, only monoolefin IV was observed as the product of the partial decomposition (*ca.* 25%) of the impure III-COOH after 12 min. at *ca.* 195°.

Mechanistic considerations lead to structure IV for the monoolefin,⁴ and this is supported by the infrared, ultraviolet (λ_{\max} 215 m μ (ϵ 7600, cyclohexane)), and n.m.r. spectra. The n.m.r. spectrum of IV in CCl₄ shows a singlet at τ 9.08 for a methyl group, a multiplet centered at τ 7.75 for 2 allylic protons, a signal at τ 4.28 for 1 vinyl proton, and an AB quartet for 2 cyclopropane protons with $J_{AB} = 5$ c.p.s., τ_A 9.32, and τ_B 9.46. Structure VI suggests itself for the diolefin,⁴ and this is in line with the infrared, ultraviolet (λ_{\max} 248 m μ (ϵ 1.97 \times 10⁴, cyclohexane)), and n.m.r. spectra. The n.m.r. spectrum in CCl₄ shows singlets at τ 9.05 and 8.98 for 2 methyl groups, signals centered at τ 4.92 and 4.30 for 2 vinyl protons, and a broad multiplet centered at τ 7.83 for 4 allylic protons.

Although no mechanistic study of the decarboxylation of III-COOH has been carried out to determine its intramolecular or intermolecular character, an intramolecular process symbolized in VII is quite attractive. The geometry of III-COOH with a relatively flat⁶ central six-membered ring seems quite favorable for such a process. The conversion of monoolefin IV to diolefin VI appears to involve a slower intermolecular action of carboxylic acid on IV. The second cyclopropane ring opens so as to lead to an allylic cation V (ion pair) or ester as an intermediate.

The intramolecular decarboxylative opening of the cyclopropane ring symbolized by VII represents a homocounterpart of the more familiar intramolecular⁷

decarboxylation of β,γ -unsaturated acids (VIII). Process VII involves a 1,5-shift of hydrogen from oxygen to carbon with opening of a cyclopropane ring, and thus there is some analogy between VII and homodienyl 1,5-shifts⁸ symbolized by IX. The relationship between VII and VIII resembles the one between homodienyl and dienyl 1,5-shifts⁸ (IX and X).



Since β,γ -cyclopropane-substituted carboxylic acids are now fairly readily accessible, the decarboxylative cyclopropane ring opening illustrated above, with stereospecific introduction of an angular methyl or other group, might well prove to be generally useful.⁹ Since two cyclopropane rings are readily introduced (*e.g.*, III-COOH), the type of transformation illustrated by III-COOH \rightarrow VI might prove useful as well.

(7) R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 4359 (1950).

(8) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963).

(9) After we had observed the behavior of III-COOH on decarboxylation we learned through Dr. Phillip Radlick that Dr. James Sims had independently proposed such decarboxylation as a conceivable synthetic method and was engaged in the investigation of a possible example. The decarboxylation of a simpler analog of III-COOH is reported by Sims in the accompanying communication [*J. Am. Chem. Soc.*, **87**, 3511 (1965)].

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Received May 24, 1965

Decarboxylation of Cyclopropylacetic Acid Derivatives. A New Synthetic Method

Sir:

The facile decarboxylation of β,γ -unsaturated carboxylic acids is well known.¹ It has been proposed that the mechanism of this reaction involves a cyclic six-membered transition state with a concerted shift of electrons.¹ We felt that it should be possible to substitute a cyclopropane ring for the double bond since cyclopropane derivatives have long been known to undergo reactions characteristic of olefinic linkages²; molecular orbital calculations^{3,4} have rationalized this similarity of reactivity. Toward that end we prepared a pair of epimeric cyclopropylacetic acid derivatives, *cis*- and *trans*-Ia, and found that both acids underwent smooth thermal decarboxylation yielding an identical olefin II. The role of the cyclopropane ring in this new decarboxylation is seen to be similar to that of the double bond in β,γ -unsaturated acids.

Decarboxylation of the acids was carried out in a distilling flask at 230–250°. *cis*-Ia gave a 90% isolated yield of a single olefin. *Anal.* Calcd. for C₈H₁₂: C, 88.82; H, 11.18. Found: C, 88.92; H, 11.14. The structure II was assigned to the olefin on the basis

(1) R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 4359 (1950), and references cited therein.

(2) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(3) C. A. Coulson and W. E. Moffit, *Phil. Mag.*, **40**, 1 (1949).

(4) D. Peters, *Tetrahedron*, **19**, 1539 (1963).

(6) (a) W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Am. Chem. Soc.*, **86**, 3126 (1964); (b) R. Boikess and J. Brauman, unpublished work.