

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°.

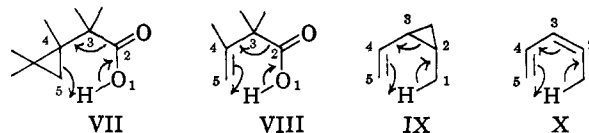
Mechanistic considerations lead to structure IV for the monoolefin,⁴ and this is supported by the infrared, ultraviolet (λ_{\max} 215 m μ (ϵ 7600, cyclohexane)), and n.m.r. spectra. The n.m.r. spectrum of IV in CCl₄ shows a singlet at τ 9.08 for a methyl group, a multiplet centered at τ 7.75 for 2 allylic 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

(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.

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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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.

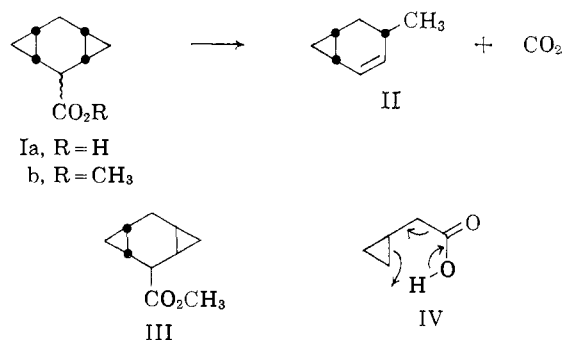
Decarboxylation of the acids was carried out in a distilling flask at 230–250°. *cis*-Ia gave a 90% isolated yield of a single olefin. *Anal.* Calcd. for C₈H₁₂: C, 88.82; H, 11.18. Found: C, 88.92; H, 11.14. The structure II was assigned to the olefin on the basis

(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).



of its analysis and infrared (λ (film) 6.10, 6.90, 9.80, and 12.85 μ) and n.m.r. spectra. The n.m.r. spectrum of the neat olefin showed the following peaks: a broad doublet, area 1, at τ 4.02 ($J = 10$ c.p.s.), a sharp doublet, area 1, at 4.37 ($J = 10$ and 4 c.p.s.), a sharp doublet, area 3, at 8.96 ($J = 7.0$ c.p.s.), a multiplet, area 1, centered at 9.95, and two remaining broad multiplets, combined area 6. Thus the spectrum can be interpreted as showing two olefinic protons (τ 4.02 and 4.37) of a disubstituted double bond, a secondary methyl group (8.96), and a cyclopropyl ring (9.95). Similar decarboxylation of *trans*-Ia gave a poorer yield of II (62% isolated) identical in all respects (infrared, n.m.r., and vapor phase chromatography) with that from *cis*-Ia.

The preparation of these acids brought to light an interesting and useful bit of knowledge concerning the Simmons-Smith reaction.⁵ When methyl 1,4-dihydrobenzoate⁶ was treated with an excess of the Simmons-Smith reagent,⁵ the major product (*ca.* 80%) was composed of two isomeric, bis adducts A and B, evidenced by vapor phase chromatography, in the relative proportions of 80% A and 20% B. If pure A, pure B, or the reaction mixture above was refluxed with a catalytic amount of sodium methoxide in dry methanol, an identical equilibrium mixture containing 30% A and 70% B was obtained. Three bis adducts could have been formed in the cyclopropanation reaction: two meso compounds, *cis*- and *trans*-Ib, and a *dl* pair III. The equilibration of A and B excludes III as a possible structure for either A or B, since such an equilibration of III would produce no new compound. Thus A and B must be the *cis* and *trans* forms of Ib. Assignment of the correct relative stereochemistry to A and B was accomplished by inspection of Dreiding models of *cis*- and *trans*-Ib, from which it was clear that the carbomethoxyl group is significantly more hindered in *cis*-Ib than in *trans*-Ib. In the analogous case of 2,5-dimethylcyclopentanecarboxylic acid, it has been shown⁷ that the all *cis* acid is less stable thermodynamically than the acid in which the two methyl groups are *trans* to the carboxyl group. On this basis isomer A is *cis*-Ib and isomer B is *trans*-Ib. When the above stereochemical result is compared with that obtained by carrying out the Simmons-Smith reaction on 1,4-dihydrobenzene, which results in the predominately *trans* configuration of cyclopropyl rings,⁸ it is seen that

(5) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4526 (1959).

(6) M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963).

(7) T. L. Jacobs and W. H. Florsheim, *J. Am. Chem. Soc.*, **72**, 256, 261 (1950).

(8) W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *ibid.*, **86**, 3126 (1964).

the carbomethoxyl group has exerted a profound directing influence on the reaction. The similar directive influence of allyl alcohols, their methyl ethers, and homoallyl alcohols has previously been observed.⁹

Careful saponification of the reaction mixture from the cyclopropanation and fractional crystallization of the mixture of acids so obtained yielded *cis*-Ia, m.p. 106–107°, $\lambda_{C=O}$ CHCl_3 5.85 μ . The n.m.r. spectrum of *cis*-Ia in CCl_4 showed the following peaks: a singlet, area 1, at τ -2.33 (acid OH), a triplet, area 1, at 6.51, $J = 6$ c.p.s. (assigned to the proton α to the carboxyl group), a multiplet, area 2, at 7.82 (assigned to the cyclohexane methylene), and two multiplets, each of area 4, at 8.6–9.2 and 9.3–10.1 (assigned to the cyclopropane protons). Saponification of the equilibrated mixture of esters from the cyclopropanation with a limited amount of potassium hydroxide produced the epimeric acid *trans*-Ia, m.p. 87–88°, $\lambda_{C=O}$ CHCl_3 5.85 μ . Its n.m.r. spectrum contained the following peaks: a singlet, area 1, at τ -2.30 (acid OH), a multiplet, area 1, at 7.45 (proton α to carboxyl group), a multiplet, area 8, from 8.2 to 9.7, and a multiplet, area 2, centered at 9.95.

The possibility that the acids Ia might equilibrate under the conditions of the decarboxylation prevents any conclusions at this time about the stereochemical requirements of the reaction. However, the relative yields of olefin from both acids compel one to consider as highly likely a cyclic transition state such as IV, at least for decarboxylation of the *cis*-acid. Experiments are currently in progress to test this hypothesis and to exploit this new, high yield decarboxylation as a synthetic tool.¹⁰

(9) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961); P. C. Radlick and S. Winstein, *ibid.*, **86**, 1866 (1964).

(10) S. Winstein and co-workers have independently observed an example of this decarboxylation. We are grateful to Professor Winstein for communication of his results prior to publication.

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The Photolysis of 2,3-Dicarbaheptaborane(8)

The compounds 1,5-dicarbaloopentaborane(5) ($\text{C}_2\text{B}_3\text{H}_5$), 1,2-dicarbaloohexaborane(6) ($1,2\text{-C}_2\text{B}_4\text{H}_6$), 1,6-dicarbaloohexaborane(6) ($1,6\text{-C}_2\text{B}_4\text{H}_6$), and 2,4-dicarbaloheptaborane(7) ($\text{C}_2\text{B}_5\text{H}_7$) have been synthesized and characterized.¹⁻³ However, further work with these carboranes has been hampered by the extremely low yields obtained, especially for the first three compounds. We have found that ultraviolet irradiation of 2,3-dicarbaheptaborane(8) ($\text{C}_2\text{B}_4\text{H}_8$) vapor gives greatly improved yields of $\text{C}_2\text{B}_3\text{H}_5$, $1,2\text{-C}_2\text{B}_4\text{H}_6$, and $1,6\text{-C}_2\text{B}_4\text{H}_6$.

(1) I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(2) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963).

(3) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).