cases, the formation of the cyclopropane ring is stereochemically specific, resulting exclusively from *cis* addition. Mechanistically the addition appears to occur in a single step without rotating intermediates.

cis-Butene is the only olefin found so far with which methylene reacts with discrimination. A possible explanation involving dipolar association prior to absorption of light and decomposition is being investigated.

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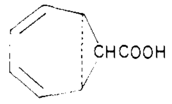
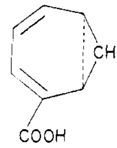
THE STRUCTURE OF THE BUCHNER ACIDS

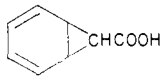
Sir:

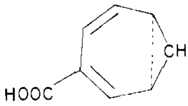
To norcaradienecarboxylic acid (I, liquid), α-(II, m.p. 71.5°), β-(III, m.p. 59.5°), γ- (IV, m.p. 64.5°; amide, m.p. 85°) and the δ- (V, m.p. 31°) cycloheptatrienecarboxylic acids, the five $C_8H_8O_2$ acids uncovered in the laboratories of Buchner and Einhorn (see Grundmann and Ottmann[1] for references), Buchner *tentatively* assigned structures Ib, IVc,[2] IIc, IIIc and Ic, respectively; DeJong,[3] structures Ib, IVc, IIIc, Ic and IIc; and Grundmann and Ottmann,[1] structures Ib, Ic, IIIc, IVc and IIc. We wish to communicate evidence by which the "δ-acid" is removed and structures Ia, IIa, IIIa and IVa are assigned to the four remaining acids.

Ia


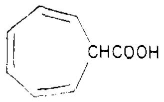


IIa
α-acid

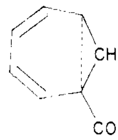
Ib




IIIa
β-acid

Ic


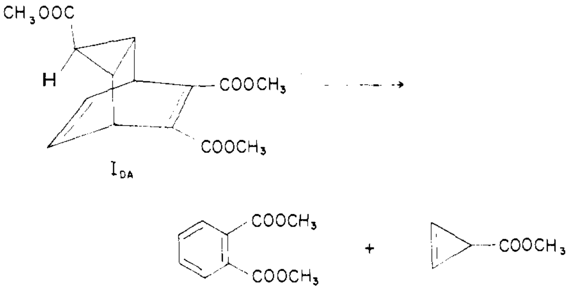
"Norcaradiene-
carboxylic acid"



IVa
γ-acid

Since V and a 47:53 mixture (m.p. 31°) of II and III have superimposable infrared spectra and since α-amide (m.p. 127°) can be crystallized from "δ-amide", "δ-acid" is non-existent.

The methyl esters ($\mathrm{I_{Me}}$, $\mathrm{II_{Me}}$, $\mathrm{III_{Me}}$ and $\mathrm{IV_{Me}}$) of the four remaining acids react with dimethyl acetylenedicarboxylate to give infrared-spectroscopically different, non-intercontaminated Diels–Alder adducts ($\mathrm{I_{DA}}$: m.p. 76°; $\mathrm{II_{DA}}$: liquid; $\mathrm{III_{DA}}$: m.p. 68°; $\mathrm{IV_{DA}}$: liquid) which all have cyclopropane structures (*e.g.*, $\mathrm{I_{DA}}$).[4] Pyrolyses at 200–300° furnish dimethyl phthalate, trimethyl benzene-1,2,3-tricarboxylate, trimethyl benzene-1,2,4-tricarboxylate and dimethyl phthalate, respectively: confirming structure I for "norcaradienecarboxylic acid," establishing structures II and III for α- and β-acids and being inconclusive about γ-acid.



In the aliphatic C–H region (displaced 27–30 milligauss [benzene 0.0], Varian Associates Nuclear Magnetic Resonance Spectrometer, 30 megacycles, 7047 gauss field strength) the NMR spectrum of $\mathrm{I_{Me}}$ shows one hydrogen atom split into a triplet by coupling with two equivalent, adjacent hydrogen atoms (in complete accord with structure I); $\mathrm{II_{Me}}$ and $\mathrm{III_{Me}}$ show two hydrogen atoms, likewise split into triplets (in accord with the assigned structures); $\mathrm{IV_{Me}}$ also shows two hydrogen atoms, which being split into a *doublet*, unequivocally implies coupling with *one* adjacent hydrogen atom. Consequently only structure IV is tenable for γ-acid.

The NMR spectra of the four methyl esters and of tropilidene are so similar and so uniquely complicated in the vinyl C–H region that one valency-tautomeric system[2] must be common to all. In an important application of NMR, Corey, Burke and Remers[5] have excluded type b (norcaradiene) as the structure for tropilidene. Similarly, none of the Buchner esters may have a type b structure. 1,3,5-Cycloöctatriene which necessarily has a *non-planar*, type c structure has only one simple NMR absorption in the vinyl C–H region and a resonance energy of 2 kcal.[6] By contrast tropilidene has an exceptionally complicated NMR spectrum and a resonance energy of 6–8 kcal.[6] It therefore seems highly probable that tropilidene and the Buchner acids have the *planar*, pseudo-aromatic type a (tropilidene) structure.

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[1] Ch. Grundmann and G. Ottmann, *Ann.*, **582**, 163 (1953).

[2] Three possible sets of valence tautomeric structures, illustrated by Ia, Ib and Ic, are designated by a, b and c.

[3] A. W. K. DeJong, *Rec. trav. chim.*, **56**, 198 (1937).

[4] K. Alder and G. Jacobs, *Ber.*, 1528 (1953), demonstrated this type of structure for the tropilidene–maleic anhydride adduct. In addition to VI, pyrolysis of $\mathrm{I_{DA}}$ gives VII (hydrogenated and saponified to cyclopropanecarboxylic acid and being investigated as a source of $C_8H_8^+$). Hexahydro $\mathrm{II_{DA}}$ and $\mathrm{III_{DA}}$ show C–CH_3.

[5] E. J. Corey, H. J. Burke and W. A. Remers, THIS JOURNAL, **77**, 4941 (1955).

[6] Professor R. B. Turner, private communication.