2-Methylsulfonylthionylaniline (XII).—To a solution in anhydrous benzene (10 ml.) of XI (0.4 g.) was added thionyl chloride (0.2 ml.) when a precipitate of amine hydrochloride separated immediately. The mixture was refluxed on the steam-bath for ten hours, when all of the amine hydrochloride was dissolved. The solvent was removed under vacuum, then petroleum ether (b.p. 30–60°) was added and removed under vacuum. This treatment was repeated until the odor of thionyl chloride had disappeared. The remaining yellow-brown solid was not removed for classification, but was used immediately in the next step.

Reaction of 2-Methylsulfonylthionylaniline with Phenylhydroxylamine.—To a solution of phenylhydroxylamine (0.6 g.) in benzene containing granular anhydrous sodium sulfate (2.5 g.) was added dropwise to a solution in benzene of the thionylamine XII prepared in the previous step. After standing four hours, the mixture was filtered, the filtrate concentrated and then chromatographed on alumina. The orange phase was collected and evaporated to dryness. After recrystallization from alcohol, 0.15 g. (25%) of 2-methylsulfonylazobenzene, m.p. 95.5–96.5°, was obtained. A mixed melting point with the methylated rearrangement product III prepared previously was 95.5–96.6° and the infrared spectra of both samples in chloroform were identical.

Anal. Calcd. for $C_{13}H_{12}O_2N_2S$: C, 59.98; H, 4.65; N, 10.77; S, 12.32. Found: C, 59.43; H, 4.68; N, 10.53; S, 10.01, 8.02.

The irregular sulfur analysis may have been due to a loss of sulfur dioxide during the analysis.

Azobenzene-2-sulfenyl Bromide (XIII).—To a solution of the base rearrangement product II (0.245 g.) in glacial acetic acid (4 ml.) was added 40% hydrobromic acid (3 ml.). The mixture was boiled for ten minutes, cooled, diluted with water (50 ml.), and extracted with chloroform. The extract was evaporated to dryness, leaving an orange-brown solid. After recrystallization from ethanol 0.12 g. (45%) of azobenzene-2-sulfenyl bromide was obtained as yellow needles, m.p. 222.5–224.5° (lit.[12] 223–224°).

Anal. Calcd. for $C_{12}H_9N_2SBr$: C, 49.16; H, 3.09; N, 9.56; S, 10.94; Br, 27.26. Found: C, 49.12; H, 3.28; N, 9.39; S, 10.67; Br, 27.42.

2-Thiocyanoazobenzene (XIV).—To a solution of azobenzene-2-sulfenyl bromide (0.1 g.) in water (20 ml.) was added slowly an aqueous solution of potassium cyanide (0.2 g.). Immediately an orange precipitate of XIV separated. The mixture was extracted with chloroform and the extract evaporated to dryness. The residue was recrystallized from petroleum ether (b.p. 30–60°), giving 0.07 g. (86%) of orange needles, m.p. 99–101° (lit.[13] 99–100°).

COLUMBUS, OHIO

COMMUNICATIONS TO THE EDITOR

THE *CIS* ADDITION OF DIBROMOCARBENE AND METHYLENE TO *CIS*- AND *TRANS*-BUTENE

Sir:

With the discovery of the addition to olefins of dichloro- and dibromocarbene to give 1,1-dihalocyclopropane derivatives[1] and of methylene to give cyclopropane derivatives,[2,3] it became important to one's understanding of the mechanism and the synthetic usefulness to determine the stereochemical characteristics of the additions. In a recent paper,[4] Skell and Garner have found that the general bromoform reaction of Doering and Hoffmann with *cis*- and *trans*-2-butene is stereospecific, although the stereochemistry remains unknown due to the failure to elucidate the structure of the products. Our results confirm the stereospecificity reported by Skell and Garner, and establish the stereochemistry to be *cis*, in the additions of both dibromocarbene and methylene.

From the reaction of *cis*- and *trans*-butene, each of 99% purity, with bromoform and potassium *t*-butoxide, *cis*-[5] and *trans*-[6] 1,1-dibromo-2,3-dimethylcyclopropanes, respectively, are obtained. Intercontamination is estimated not to exceed 1% by gas chromatographic analysis (Perkin–Elmer Model 154, Column "A," 10 lb., He, 145°). Reduction with sodium and methanol in tetrahydrofuran affords *cis*-[7] and *trans*-[8] 1,2-dimethylcyclopropanes, respectively, having infrared spectra identical with those of authentic samples[9] and showing less than 1% intercontamination. The configurations of *cis*- and *trans*-1,2-dimethylcyclopropane have been assigned by Baudrenghien[10] using the Auwers–Skita rule, quite valid here where the rigid ring system allows unequivocal assignment of the lower dipole moment and therefore lower boiling point to the *trans*-isomer. Accordingly the two dibromodimethylcyclopropanes have the configurations assigned above. The exclusively *cis* mode of addition makes available a two-step method for the preparation of cyclopropane derivatives having the same configurations as those of the olefins from which they are derived. Mechanistically the *cis* addition is inconsistent with initial addition of the tribromomethide ion and supports the direct addition of dibromocarbene to the olefin without benefit of intermediates. The electron demands of the transition state are being determined by competition experiments and variation in the olefin structure.

When *cis*- and *trans*-butene are irradiated with diazomethane[3] and the products are examined gas chromatographically and infrared spectroscopically, no isomerization of the starting olefins can be detected. At −75 and −5°, respectively, *cis*-butene leads to *cis*-1,2-dimethylcyclopropane containing less than 1% of other C_5 products, whereas *trans*-butene leads to *trans*-1,2-dimethylcyclopropane (27 and 35%), *trans*-pentene-2 (59 and 46%) and 2-methylbutene-2 (14 and 19%). Despite the extraordinary reactivity and general lack of discrimination usually shown by methylene,[3] in both

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(1) W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

(2) Cf. ref. 1, footnote 10.

(3) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

(4) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

(5) B.p. 85.5° at 50 mm.; m.p. −53°; n^{30}_D 1.5150; d^{30}_4 1.7513; C, 26.45; H, 3.61; Br, 70.17; 2.24 D.

(6) B.p. 81.8° at 50 mm.; m.p. −32.5°; n^{30}_D 1.5074; d^{30}_4 1.7298; C, 26.42; H, 3.72; Br, 69.99; 2.24 D.

(7) B.p. 37.0°; n^{20}_D 1.3856 (reported[9] b.p. 37.03°; n^{20}_D 1.3830).

(8) B.p. 28.2°; n^{20}_D 1.3701 (reported[9] b.p. 28.20°; n^{20}_D 1.3710).

(9) R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord. THIS JOURNAL, **77**, 1751 (1955), who very kindly furnished infrared spectra of authentic samples.

(10) J. Baudrenghien, *Bull. soc. chim. Belg.*, **38**, 172 (1929).

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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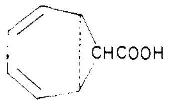
RECEIVED AUGUST 15, 1956

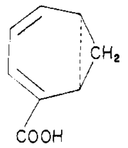
THE STRUCTURE OF THE BUCHNER ACIDS

Sir:

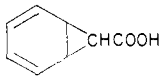
To norcaradienecarboxylic acid (I, liquid), α-(II, m.p. 71.5°), β-(III, m.p. 59.5°), γ- (IV, m.p. 64.5°; amide, m.p. 85°) and the δ- (V, m.p. 31°) cycloheptatrienecarboxylic acids, the five $C_8H_8O_2$ acids uncovered in the laboratories of Buchner and Einhorn (see Grundmann and Ottmann[1] for references), 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.



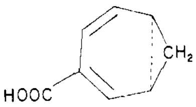
Ia



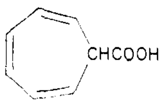
IIa
α-acid



Ib

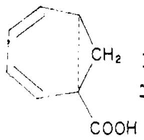


IIIa
β-acid



Ic

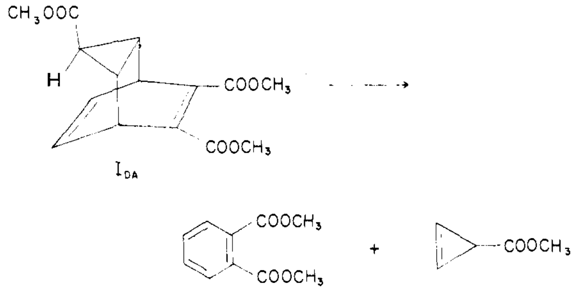
"Norcaradiene-carboxylic acid"



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 (I_{Me}, II_{Me}, III_{Me} and IV_{Me}) of the four remaining acids react with dimethyl acetylenedicarboxylate to give infrared-spectroscopically different, non-intercontaminated Diels–Alder adducts (I_{DA}: m.p. 76°; II_{DA}: liquid; III_{DA}: m.p. 68°; IV_{DA}: liquid) which all have cyclopropane structures (*e.g.*, 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.



I_{DA}

VI

VII

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 I_{Me} shows one hydrogen atom split into a triplet by coupling with two equivalent, adjacent hydrogen atoms (in complete accord with structure I); II_{Me} and III_{Me} show two hydrogen atoms, likewise split into triplets (in accord with the assigned structures); 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 I_{DA} gives VII (hydrogenated and saponified to cyclopropanecarboxylic acid and being investigated as a source of $C_3H_5^+$). Hexahydro II_{DA} and 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.