

using the shift in the ultraviolet spectrum in alkali to determine the extent of dealkylation. The mixture was cooled, diluted with water, and the precipitate which formed was filtered off. The precipitate was dissolved in 40 ml. of ethanol and the solution was run through a column containing charcoal (2 g.) and Celite (4 g.). The column was washed with 150 ml. of ethanol and the total eluate was evaporated. Recrystallization of the residue from aqueous ethanol yielded 0.54 g. (3.6 mmoles, 31%) of compound XVIII in the form of white platelets, m.p. 212–214°.

D-Luciferin.—D-Cystine (364 mg., 1.51 mmoles) was dissolved in liquid ammonia (70 ml.) and reduced with sodium; small pieces were added until the blue color persisted for 10 minutes, at which time the excess was destroyed with ammonium chloride. The ammonia was allowed to evaporate in a current of nitrogen. The residue was dissolved in 10 ml. of water saturated with nitrogen and the pH of the solution was adjusted to approximately 8 with 1 *N* hydrochloric acid (8 ml.) and 1 *N* sodium hydroxide (3 ml.). This solution of cysteine was added to a solution of 2-cyano-6-hydroxybenzothiazole (503 mg., 2.88 mmoles) in 20 ml. of methanol saturated with nitrogen and the mixture was kept under nitrogen in a flask of low-actinic glass for 0.5 hour. The precipitate which formed first redissolved. The solution was filtered from traces of the precipitate that remained, acidified with 1 *N* hydrochloric acid (4 ml.) and allowed to stand overnight at 4°. Filtration yielded 0.743 g. (2.65 mmoles, 94%) of luciferin in the form of yellow needles, m.p. 189–190.5° dec. Paper chromatography showed this material to be contaminated with a blue-green fluorescent material with R_f 0.84. A portion of the crude product (83 mg.) was recrystallized rapidly from 7 ml. of methanol to give a sample (44 mg., 50%), m.p. 189.5–190° dec., $[\alpha]^{22D} -36^\circ$ (c 1.2, dimethylformamide) which contained only a trace of impurities as shown by paper chromatography. See Table I for the ultraviolet spectrum. The infrared, ultraviolet and fluorescence spectra of synthetic D-luciferin were identical with those of natural luciferin; a comparison of the paper chromatographic behavior and the enzymatic reactivity²⁸ also showed that the two luciferins were identical.

Anal. Calcd. for $C_{11}H_8N_2O_3S_2$: C, 47.14; H, 2.85; N, 10.00; S, 22.88. Found: C, 47.36; H, 3.13; N, 9.96; S, 22.96, 22.97.

The L- and DL-luciferins were prepared directly from L- and DL-cystine in a similar fashion.

6-Methoxybenzothiazole-2-thiocarboxamide (XXI).—2-Cyano-6-methoxybenzothiazole (1 g., 5.3 mmoles) was dissolved in a mixture of pyridine (20 ml.) and triethylamine (0.75 ml.), and hydrogen sulfide was bubbled through the solution for 3 hours. The solution was then diluted with water (20 ml.) and cooled on ice. The precipitate was collected and washed with water to give thionamide XXI (1.13 g., 5 mmoles, 95%), m.p. 197–198°. A sample was purified by three recrystallizations from methanol; m.p. 196–198°; λ_{max} 354.5 μ (ϵ 13,700), 318 (sh) (ϵ 9,600), 270 μ (ϵ 7,600) and 265 μ (ϵ 6,200).

Anal. Calcd. for $C_9H_8N_2OS_2$: C, 48.20; H, 3.56; N, 12.49; S, 28.60. Found: C, 48.25; H, 3.54; N, 12.44; S, 28.68.

Dimethyldehydrociferin (XXIII).—6-Methoxybenzothiazole-2-thiocarboxamide (2.0 g., 9.0 mmoles), methyl bromopyruvate (5.4 g., 30 mmoles) and absolute methanol (200 ml.) were stirred together at room temperature for 22 hours and then heated under reflux for 17 hours. The mixture was cooled to 0° and filtered to yield 2.48 g. (7.9 mmoles, 88%) of the condensation product, m.p. 233–235.5°. For analysis, it was recrystallized three times from acetone and sublimed *in vacuo*; m.p. 233–235°, λ_{max} 348 μ (ϵ 23,400) and 274 μ (ϵ 9,600).

Anal. Calcd. for $C_{13}H_{10}N_2O_3S_2$: C, 50.96; H, 3.29. Found: C, 50.96; H, 3.27.

Dehydrociferin (XI)—Dimethyl dehydrociferin (0.69 g., 2.2 mmoles) was heated under reflux with concentrated hydrobromic acid (25 ml.) for 1.5 hours. The solution was cooled and poured into 100 ml. of water. The dark olive-colored precipitate (0.56 g.) was collected and then treated in dimethylformamide (5 ml.) with 50 mg. of charcoal. The treated extracts were heated, diluted with 10 ml. of water, and cooled slowly. Filtration yielded the crude product, which was treated again with charcoal to yield a light greenish-yellow solid weighing 0.35 g. This material was crystallized from a dimethylformamide–water mixture, then dissolved in methanol containing aqueous sodium hydroxide and precipitated with dilute hydrochloric acid. The product, dehydrociferin, was obtained as a yellow, crystalline solid (0.13 g., 0.47 mmole, 20%) melting at 315–321° dec. and showing a single spot on paper chromatography; λ_{max} 350 μ (ϵ 24,000), 275 μ (ϵ 8,800) and 271 μ (ϵ 8,800).

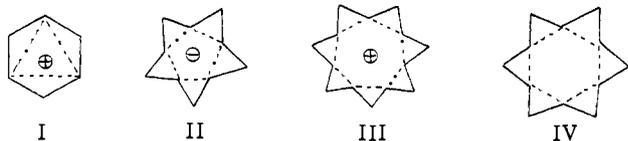
Anal. Calcd. for $C_{11}H_8N_2O_3S_2$: C, 47.47; H, 2.17; N, 10.07; S, 23.04. Found: C, 47.40; H, 2.34; N, 10.19; S, 22.84.

COMMUNICATIONS TO THE EDITOR

THE HEXAHOMOBENZENE PROBLEM. TETRACYCLO-[9.1.0.0.0^{3,8}0^{7,9}]DODECANE

Sir:

Evidence was reported recently in favor of a non-classical trishomocyclopropenyl structure (I) for the 3-bicyclo[3.1.0]hexyl cation.¹ Further, it was suggested that the homo-relationship of this ion to the cyclopropenyl cation might be generalized to include homo-counterparts of other aromatic molecules.^{1,2} On this basis, conceivable homoaromatic species are the pentahomocyclopentadienide and heptahomotropylium ions II and III, and even the neutral hexahomobenzene IV was considered as a possibility.



In the course of synthetic approaches to systems with the spacing and stereochemistry of cyclopropane rings required to test these ideas, a shortcut to "hexahomobenzene" presented itself when *cis-cis-cis*-1,4,7-cyclononatriene³ became available to us. Thus, we now can report the preparation and properties of the pertinent compound, *cis*-tetracyclo[9.1.0.0^{3,8}0^{7,9}]dodecane.

(1) S. Winstein and J. Sonnenberg *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(2) S. Winstein, *ibid.*, **81**, 6524 (1959).

(3) P. Radlick and S. Winstein, *ibid.*, **85**, 344 (1963).

When *cis-cis-cis*-1,4,7-cyclononatriene³ (V) was subjected to the Simmons–Smith reaction,⁴ employing 10 equivalents of methylene iodide and a 12 hour reaction time, vapor phase chromatography indicated complete disappearance of the starting material. The reaction mixture contained a number of products, but one predominated quite largely (80–90%). Conventional work-up afforded an oil which solidified on cooling. Purification by fractional melting and sublimation at 65° and 60 mm. yielded thin white needles, m.p. 54–57°. The vapor phase chromatogram of this material on a column of XF1150 Nitrile Silicone (F and M Scientific Corp., Avondale, Pa.) indicated it to be a 97:3 mixture of two materials. Vapor phase chromatographic separation of the major component yielded material, m.p. 60–62°. The C,H-analysis and molecular weight of this material are consistent with the formula $C_{12}H_{18}$ for a *tris*-methylene adduct of the original cyclononatriene.

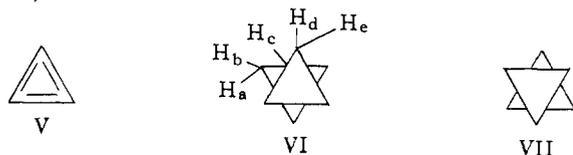
Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18; mol. wt., 162. Found: C, 88.61; H, 11.11; mass spectral⁵ parent peak, 162.

As regards the structure of the $C_{12}H_{18}$ hydrocarbon, its infrared and proton magnetic resonance spectra show it to be saturated and to possess distinct cyclopropane and "ordinary" alicyclic methylene groups as

(4) (a) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); (b) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

(5) We are indebted to Dr. Richard Teeter of the California Research Corporation for the mass spectrum determination.

in VI. Thus, in its infrared spectrum, the hydrocarbon has five strong bands in the C-H stretching region, consistent with symmetric and asymmetric stretches of both kinds of methylene groups and a *tertiary* cyclopropane C-H stretch. The observed bands occur at 2840 (symmetric "ordinary" methylene stretch), 2900, 2942, 2990 and 3058 cm^{-1} (asymmetric cyclopropane methylene stretch). Also, the hydrocarbon displays two methylene scissoring bands at 1465 and 1450 cm^{-1} , respectively. Other pertinent strong bands occur at 1020, 1010 and 848 cm^{-1} .



The proton magnetic resonance spectrum (Varian A-60) of the $\text{C}_{12}\text{H}_{18}$ hydrocarbon in carbon tetrachloride solution with hexamethyldisiloxane as an internal standard shows three bands: (i) a doublet centered at 7.84 τ ($J = 13$ c.p.s.) with very slight additional splitting of each member of the doublet; relative area 2.99; (ii) a broad complex multiplet centered at 9.32 τ ; relative area 12.1; (iii) an apparent pentuplet (with further additional fine structure) centered at 10.41 τ ; relative area 2.93. The signal from 3 protons at $\tau = 10.41$ is indicative of three cyclopropane rings, since cyclopropane rings fused to other rings commonly⁶ show one methylene proton (H_a) at τ above 10 and the other three at τ ca. 9.3. On this basis, 9 of the 12 protons responsible for the broad band at $\tau = 9.32$ are the 3 other cyclopropane methylene protons (H_b) and the 6 *tertiary*-cyclopropane protons (H_c). The remaining 3 of the 12 protons must be three of the "ordinary" methylene hydrogens (H_e), while the three remaining methylene protons (H_d) must be responsible for the signal at $\tau = 7.84$. Such discrimination between allycyclic methylene protons adjacent to a cyclopropane ring is usual,⁶ one proton being shielded and the other deshielded.

The observed pattern of bands in the proton magnetic resonance spectrum of the $\text{C}_{12}\text{H}_{18}$ hydrocarbon points to a *cis*-arrangement of the three cyclopropane rings in VI. With this arrangement, the three "ordinary" methylene groups each have one proton *cis* and one proton *trans* to two cyclopropane rings, consistent with the observed 3:3 split of these hydrogens. In the *trans*-isomer of VI, only one methylene group bears such a pair of protons, while the other two have four equivalent protons.⁷

The present evidence is that, even in the favorable isomer of VI, delocalization and compression energies do not blend in a way conducive to a homoaromatic structure (IV) under ordinary conditions. Isotopic labeling experiments are currently in progress to study the possible valency tautomerism $\text{VI} \rightleftharpoons \text{VII}$. Also, work is continuing on the syntheses of the more likely homoaromatic ionic species II and III.

(6) P. Radlick, R. Boikess and E. Friedrich, unpublished work.

(7) An illustrative example is provided by the *bis*-dideuteriomethylene adducts of 1,4-cyclohexadiene.⁸ The *trans*-isomer shows methylene and *tertiary*-cyclopropane bands in a 4:4 ratio, while the *cis*-isomer shows methylene and combined methylene-*tertiary*-cyclopropane bands in a 2:6 ratio.

(8) National Science Foundation Post-Doctoral Fellow, 1962-1963.

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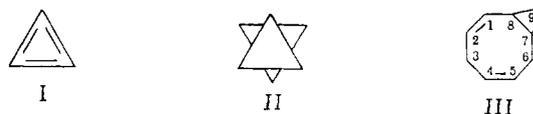
RECEIVED NOVEMBER 26, 1962

cis-cis-cis-1,4,7-CYCLONONATRIENE, A
HOMOCONJUGATED SIX π -ELECTRON SYSTEM¹

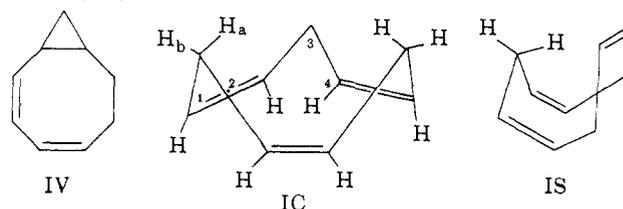
Sir:

Hydrocarbon I, *cis-cis-cis*-1,4,7-cyclononatriene, is of considerable interest in this Laboratory, mainly as a

stepping stone to "hexahomobenzene" (II),² but also as a conceivably homoconjugated six π -electron system.² We have come upon it during treatment of cyclooctatrienes with the Simmons-Smith³ reagent in the course of other syntheses and are prompted⁴ to report its preparation and its properties.



Hydrocarbon I, m.p., 49.5-50.0°, was first obtained in 30% yield, based on reacted starting material, when the product from treatment of 1,3,6-cyclooctatriene⁵ with a 1.5 mole proportion of methylene iodide and excess zinc-copper couple³ was subjected to vapor phase chromatography using a stainless steel preheater at 240°. It may also be prepared by passing either the crude reaction product or a mono-adduct fraction from the Simmons-Smith reaction through a stainless steel tube packed with stainless steel shavings at 240° in an atmosphere of helium, and then separating compound I by preparative vapor phase chromatography on a 4-methyl-4-nitropimelonitrile column at 100°. While it is not clear how hydrocarbon I arises, it is quite easy to visualize its formation from a mono-adduct (III) by $\text{C}_7\text{-C}_8$ bond rupture and 9 \rightarrow 8 hydrogen shift. However, compound I appears to be formed also from IV, since similar yields of I are obtained when 1,3,5-cyclooctatriene⁵ is substituted for the 1,3,6-isomer in the above preparations.



Hydrocarbon I displays the correct C,H-analysis and mass spectral molecular weight⁶ (120) for the formula C_9H_{12} . That the substance is indeed *cis-cis-cis*-1,4,7-cyclononatriene is clear from its infrared, proton magnetic resonance and ultraviolet spectra. In the infrared, I displays bands at 3018 (s), 2965 (m), 2932 (m), 2916 (m) and 2864 (mw) cm^{-1} in the C-H stretching region, peaks at 1675 (vw) and 1641 (cm^{-1}) in the $\text{C}=\text{C}$ stretching region, a *cis*-olefinic C-H out-of-plane deformation band at 717 (s) cm^{-1} and no bands corresponding to the C-H out-of-plane and in-plane deformation bands characteristic of *trans*-olefins. In carbon tetrachloride solution with the Varian A-60 instrument, the proton magnetic resonance spectrum of I at higher temperatures, e.g., 65°, shows two proton signals centered at 4.66 and 7.10 τ , respectively,⁷ with relative peak areas of 6.0:6.0. The former value is a relatively

(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) (a) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

(3) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(4) We have learned through Dr. Aksel Bothner-By that this same hydrocarbon has been prepared through a very different route by Dr. Kar Untch of the Mellon Institute [K. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963)]. We understand also that Dr. W. Roth of the University of Cologne in Germany has come upon this hydrocarbon during the study of "thermal reorganization" reactions [W. Roth, private communication], but we were not informed which hydrocarbons were involved in these reorganizations.

(5) A. C. Cope, et al., *J. Am. Chem. Soc.*, **72**, 2515 (1950); **74**, 486 (1952).

(6) We are indebted to Dr. Richard Teeter of the California Research Corporation for the mass spectrum of this substance.

(7) With the Varian HR-40 instrument the vinyl signal appears as nonet and the methylene as at least an octet.