$^1H_{10}{}^2D^+$ ion. The 32.1-MHz ^{11}B nmr spectrum (THF solution) contains two doublets (δ +52.8 ppm relative to $BF_3O(C_2H_5)_2$, J = 180 cps, area 1; δ +2.5, J = 157 cps, area 2), assigned to the coupling of terminal hydrogen atoms with apex and base borons, respectively. The low-field doublet shows no secondary splitting,[1] confirming that the molecule is bridge deuterated. For comparison, the ^{11}B nmr spectrum of isotopically normal 2,4-$(CH_3)_2C_3B_3H_5$ in THF contains doublets of area 1 (δ +51.6 ppm, J = 178 cps) and area 2 (δ +2.5 ppm, J = 157 cps), with each peak of the low-field doublet further split (J = 49 cps) due to coupling of the two basal boron atoms with the bridge proton.[1]

The tricarbahexaborate(1−) ion presumably contains a basal C_3B_2 ring having three delocalized electron pairs, as does $C_5H_5^-$, and therefore in principle should be capable of π bonding to transition metal atoms to form analogs of the metallocenes and the dicarbollyl complexes. However, reactions of the sodium salts of 2,3- and 2,4-$(CH_3)_2C_3B_3H_4^-$ with anhydrous $FeCl_2$ and $Mn_2(CO)_{10}$ are complex, involving partial decomposition of the carborane ions. Studies of reactions of this type are proceeding and will be reported subsequently.

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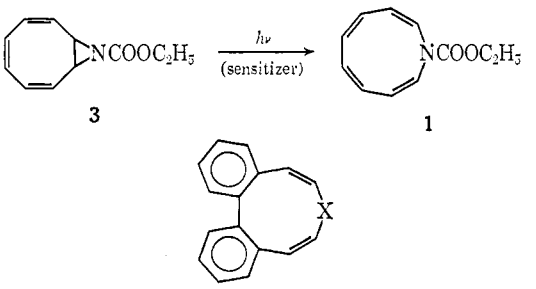
N-Carbethoxyl-1-azacyclonona-2,4,6,8-tetraene

Sir:

We have, for some time, been interested[1,2] in azacyclonona-2,4,6,8-tetraene as it represents a "4n + 2" (n = 2) π-electron homolog of pyrrole.

Hückel theory clearly predicts π-electron stability for this substance[1] while analogy with the already known[3-5] iso-π-electronic, nine-membered monocycle, cyclononatetraenide suggests that perhaps in the all-*cis* arrangement π-electron stabilization of the compound may more than compensate for the obvious energetic disadvantage due to angle strain. For these reasons, interest in the synthesis of 10π-electron heteromonocycles has been quite extensive in recent years. To date, however, pertinent reports deal solely with the synthesis of dibenzoxonin (**2a**) and dibenzothionin (**2b**)[6] and the postulated intermediacy of oxonin upon photolysis of the epoxide of cyclooctatetraene.[7] Presently we briefly describe the synthesis of **1**, the *first* parent 10π-electron heteromonocycle, and for that matter the first isolable uncharged 10π monocycle.



2a, X = O
b, X = S

1 was synthesized along the lines first suggested by us[2] on the basis of orbital symmetry.[1] Thus, brief (1 hr) through-Pyrex illumination of a cold (0°) ether solution of **3** in the presence of benzophenone, with a Hanovia light source produces a mixture, the nmr spectrum of which displays, besides absorption due to benzophenone and **3**, an AB quartet with doublet components centered at τ 3.6 (2 H) and 4.7 (2 H) (J = 10 cps) and a fairly narrow multiplet at 4.2 (4 H).[8] The position and relative areas of these signals are uniquely consistent with a fully unsaturated monocycle. Furthermore, the product, though moderately stable at 0°, is thermally unstable at room temperature, undergoing valence tautomerism to what appears to be N-carbethoxy-8,9-dihydroindole. The thermolysis of **1** is conveniently monitored by nmr at room temperature, the aforementioned signals disappearing with the concurrent appearance of absorptions expected of a dihydroindole structure.

Secure chemical evidence for structure **1** derives from the following experiments. Treatment of the crude photolysis mixture ([**1**]/[**3**] ~ 1) with diimide at either 0 or −78°[9] produced a mixture of partially hydrogenated products. This was subsequently subjected to catalytic (Rh–C) hydrogenation at atmospheric pressure and room temperature to produce fully hydrogenated (nmr) components. Perhydro-**1**,(**4**), was identified both by its nmr spectrum in the mixture and the ir of a pure sample collected gas chromatographically. In both cases identification rests on direct spectral comparison with authentic **4** prepared from azacyclononane and ethyl chloroformate. In either run however it was noticed that the ratio of **4** to hydrogenated **3** was slightly larger than that of their respective dehydro precursors **1** and **3**. This piece of information suggested that perhaps **3** does produce a small amount of **4** under the reductive treatment. A control experiment employing **3** and benzophenone but no **1** demonstrated that this is indeed the case, the proportion of **4** to hydrogenated **3** in the product mixture being determined at *ca.* 1:9. Entirely definitive structural proof for **1** derives from direct low-temperature (0°), catalytic (Rh–C) hydrogenation of the photolysis mixture ([**1**]/[**3**] ~ 1) to produce a 1:1 mixture (nmr, gc) of **4** and hydrogenated **3**. Significantly, catalytic hydrogenation of a mixture of **3** and benzophenone under identical conditions produced no detectable amount (<4%) of **4**.

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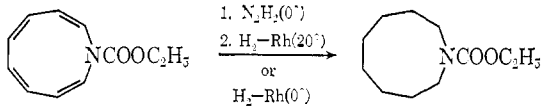
(8) Note that the nmr spectrum of the photoproduct is entirely analogous to that of **2a** which displays, besides aromatic absorption, an AB quartet with doublet components centered at τ 3.95 (2 H) and 4.70 (2 H).[6]
(9) Generated essentially by the procedure described by E. E. Van Tamelen and T. L. Burkoth *J. Am. Chem. Soc.*, **89**, 151 (1967).



1 4

All the preliminary information presented herein unequivocally points to structure **1** for the photolysis product. Furthermore, the nmr data coupled with the pronounced thermal instability displayed by this compound attest to a nonaromatic, classical polyenic, character. The compound thus appears to lack aromaticity in spite of an all-*cis* geometry clearly implicated by the nmr data.[10] We are currently concentrating our efforts toward isolating **1** in the pure form in order to secure additional spectral and chemical information concerning its aromatic or classical character.[11]

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(10) To be sure, the nmr spectrum of this substance is consistent with any structure that possesses either a plane or a rotating axis of symmetry containing the nitrogen atom and bisecting the remote C–C bond. Among these, only the all-*cis* arrangement, shown in 1, ought to possess a reasonably stable σ frame. A "Dreiding" molecular model clearly points to a puckered all-*cis* arrangement possessing a twofold rotating axis of symmetry (C_2).

(11) NOTE ADDED IN PROOF. Subsequent to submittal of this paper, 1 was obtained pure by means of low-temperature column chromatography. We shall elaborate on the purification as well as the thermal and photochemical behavior of 1 in a subsequent report.

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Stereochemistry of Tritium at Carbon 15 in Cholesterol Derived from (3*R*,2*R*)-2T-Mevalonic Acid in Rat Livers

Sir:

Recent studies on the biosynthesis of sterols have centered on the changes occurring at C-7 and C-15 during the conversion of lanosterol to cholesterol. Canonica, *et al.*,[1,2] showed that the removal of the 14α-methyl group is accompanied by loss of the 15α-hydrogen which originates from the *pro*-2*S*-proton of mevalonic acid. Later work by Gibbons, *et al.*,[3] has confirmed this observation. Subsequently, it has been demonstrated that both 4,4-dimethylcholesta-8,14-dien-3β-ol[2] and cholesta-8,14-dien-3β-ol[4,5] are converted to cholesterol by rat liver preparations. More definitive evidence of the participation of 8,14-diene intermediates has been presented by Watkinson and Akhtar,[6] with the isolation of 4,4-dimethylcholesta-8,14-dien-3β-ol during cholesterol biosynthesis in rat livers. The same group[7] have shown that in the saturation of the Δ^{14}-double bond of the 8,14-diene, the 14α-hydrogen is derived from NADPH, and the C-15 hydrogen from a proton source. In this communication we concern ourselves with the stereochemical fate of the hydrogen at C-15, originating from the *pro*-2*R*-hydrogen of mevalonic acid.

Cholesterol (I) [7.2 $\times$ 10^5 dpm ^{14}C; T/^{14}C ratio 10.1; atomic ratio (ar) 5.00:5] biosynthesized from (3*R*,2*R*)-[2T-2-^{14}C]mevalonic acid in rat livers,[8] was incubated with a bovine adrenal mitochondrial preparation.[9] The crude residue from the reaction was fractionated by thin layer chromatography (tlc) in two systems and the zone corresponding to pregnenolone (II) was isolated. The extract (4.42 $\times$ 10^4 dpm ^{14}C) was diluted with inactive pregnenolone (100 mg) and crystallized to constant specific activity (85 mg; 2.89 $\times$ 10^4 dpm ^{14}C; T/^{14}C ratio 9.8; ar 2.91:3). Oppenauer oxidation of this material gave progesterone (III) (58 mg; 2.00 $\times$ 10^4 dpm ^{14}C; T/^{14}C ratio 9.1; ar 2.70:3). Progesterone derived by Jones oxidation of 20α-hydroxypregn-4-en-3-one, a by-product of the incubation, had a T/^{14}C ratio of 9.8 (ar 2.91:3). The small loss of tritium in the progesterone obtained by Oppenauer oxidation is not clear but probably involves some loss of isotopic hydrogen from the allylic C-7 position in pregnenolone.

The radioactive progesterone (T/^{14}C ratio 9.1) was then incubated with *Calonectria decora*[10] to yield 12β,15α-dihydroxyprogesterone (IV)[11] (1.46 $\times$ 10^4 dpm ^{14}C), which had a T/^{14}C ratio of 6.2 (ar 1.84:3). In view of the earlier error[10] in the assignment of configuration at C-15, we confirmed the identity of the product as the 12β,15α-diol (IV) by its failure to undergo acid-catalyzed dehydration to a Δ^{14} compound[12] and from the chemical shift of the 18-methyl group (47 cps) in the nmr spectrum. Conclusive proof of the structure was derived from the fact that hydroxylation of stereospecifically labeled (15β-T)-(4-^{14}C)-progesterone (T/^{14}C ratio 10.8) with *Calonectria decora* gave (15β-T)-(4-^{14}C)-12β,15α-dihydroxyprogesterone (T/^{14}C ratio 10.5) which retained all the tritium. Controlled oxidation of IV with restricted amounts of Jones reagent gave 12β-hydroxypregn-4-en-3,15,20-trione (V)[11] (T/^{14}C ratio 6.6; ar 1.96:3). The assignment of structure V, rather than the alternative 15α-hydroxypregn-4-ene-3,12,20-trione structure VI, follows from the appearance of a peak at 1747 cm^{-1} (five-membered cyclic ketone), due to the C-15 ketone, in the ir spectrum, and the occurrence of the 12β-hydroxyl signal at low field (275 cps), due to hydrogen bonding between the hydroxyl and the C-20 ketone, and the shift of the 18-methyl group (49 cps), in the nmr spectrum. Complete oxidation of IV with Jones reagent gave pregn-4-ene-3,12,15,20-tetraone (VII)[11] (T/^{14}C ratio 6.4; ar 1.90:3).

The unchanged T/^{14}C ratio of the 12β-hydroxy-

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(12) We have shown that under analogous conditions, 15β-hydroxy compounds in the pregnane series (prepared by sodium borohydride reduction of the corresponding ketones) undergo a very facile dehydration to the Δ^{14} compounds (to be published).