substituted olefins derived from *symmetrical* acetylenes[8,9] but have not been applied to the *specific* synthesis of more highly substituted olefins from *unsymmetrical* acetylenes.

Studies are now in progress on the extension of this approach to olefin synthesis from acetylenes to other substrates and other reagents and on the fundamental mechanistic features of the reactions which are involved.[10]

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(8) G. Wilke and H. Mueller [*Chem. Ber.*, **89**, 444 (1956); *Ann.*, **629**, 222 (1960)] have introduced the use of dialkylaluminum hydrides for the synthesis of olefins by *cis*-hydroalumination followed by hydrolysis.

(9) (a) G. Zweifel and C. C. Whitney [*J. Am. Chem. Soc.*, **89**, 2753 (1967)] have recently described the synthesis of vinylic halides by halogenation of the organoaluminum intermediates obtained by the addition of diisobutylaluminum hydride to 1- and 3-hexyne. (b) G. Zweifel and R. B. Steele [*ibid.*, **89**, 2754 (1967)] have further extended the utility of vinylaluminum intermediates from hydroalumination to include the reaction of these intermediates and their "ate" complexes with carbon dioxide, formaldehyde, and acetaldehyde. A method proposed by Zweifel and Steele for the specific synthesis of olefins of type R'R''C=CHX from R'C≡CH and R''$_3$Al (but not actually demonstrated by application) would appear to be ineffective from the work of T. Mole and J. R. Surtees [*Chem. Ind.* (London), 1727 (1963)].

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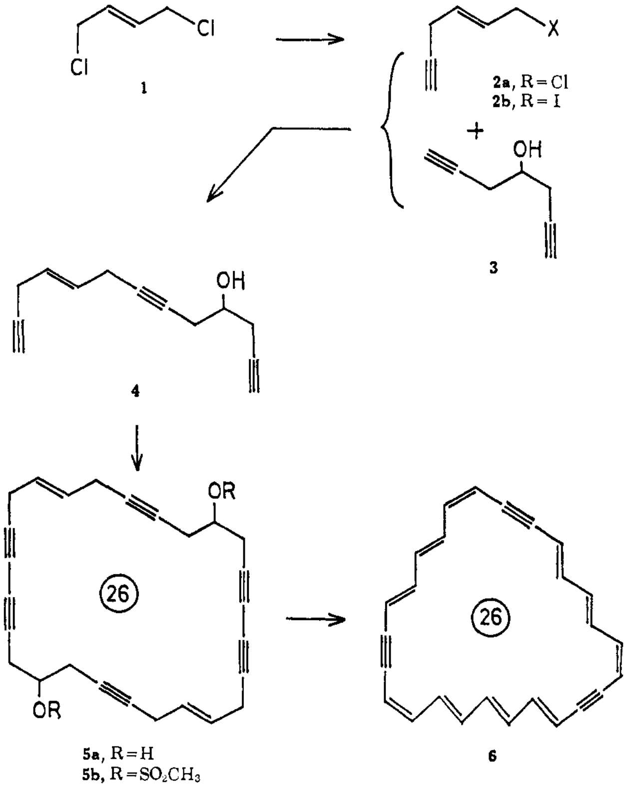
Tridehydro[26]annulene[1]

Sir:

It has been predicted that monocyclic conjugated polyenes (annulenes) containing $(4n + 2)$ π electrons will be aromatic, provided the ring size is below a certain limit.[2] Specifically, Dewar and Gleicher[2d] have calculated that [22]annulene ($n = 5$) will be aromatic, while [26]annulene ($n = 6$) will no longer be aromatic.

We have attempted to test this prediction experimentally by preparing and studying dehydro[22]-annulenes and dehydro[26]annulenes. Dehydroannulenes rather than annulenes were chosen, since it has been found in many instances that the former are superior to the latter for investigating the possible aromaticity of conjugated macrocyclic systems by nmr spectroscopy (due to the fact that the nmr spectra of dehydroannulenes are less prone to be temperature dependent than those of the more "mobile" annulenes).[3] The theoretical considerations apply equally to the annulenes and the corresponding dehydroannulenes as regards the out-of-plane π electrons. We now describe the synthesis of a tridehydro[26]annulene (*e.g.*, **6**), and present nmr evidence that this substance is not aromatic, in agreement with theory.

Reaction of *trans*-1,4-dichloro-2-butene (**1**) with ethynylmagnesium bromide[4] (0.5 molar equiv) in tetrahydrofuran in the presence of cuprous chloride[5] led to *trans*-1-chloro-2-hexen-5-yne (**2a**). This substance could not be separated readily by distillation, and the crude product was therefore stirred with sodium iodide in acetone. The resulting *trans*-1-iodo-2-hexen-5-yne (**2b**) [40% over-all yield; bp 56–57° (3.5 mm); mol wt 205.958[6]][7] on treatment with (1,6-heptadiyn-4-ol)-dimagnesium dibromide[8] in tetrahydrofuran in the presence of cuprous chloride[5] yielded 63% of *trans*-9-tridecene-1,6,12-triyn-4-ol (**4**) [bp 113–115° (0.15 mm); mol wt 186.105[6]].[7] Oxidative coupling of this compound with oxygen, cuprous chloride, and ammonium chloride in aqueous ethanol and benzene[9] for 1 hr at 55° gave a mixture of substances from which the symmetrical 26-membered cyclic "dimer" **5a** [colorless crystals, mp 166° dec;[10] mol wt 368;[6] $\lambda_{\max}^{\text{ether}}$ 240 mμ (ϵ 930) and 254 (640)] was isolated by chromatography in 6% yield.



The cyclic dimer was shown to possess the symmetrical 1,14-dihydroxy structure **5a** (rather than the other possible, unsymmetrical, 1,8-dihydroxy structure) since catalytic hydrogenation in dioxane over platinum and subsequent oxidation with Jones reagent led to 1,14-cyclohexacosanedione (mp 66–68°), identified by direct comparison with an authentic sample (mp 67–68°).[11]

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(1) Part L in the series "Unsaturated Macrocyclic Compounds." For part IL, see K. Grohmann and F. Sondheimer, *Tetrahedron Letters*, in press.

(2) (a) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), **A251**, 172 (1959); (b) *ibid.*, **257**, 445 (1960); (c) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962); (d) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(3) For reviews, see (a) F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967); (b) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, in press.

(4) E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); *Org. Syn.*, **39**, 56 (1959).

(5) See J. P. Danehy, D. B. Killian, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 611 (1936).

(6) The molecular weight values were determined by mass spectroscopy (AEI MS9 spectrometer).

(7) The substance showed nmr and infrared spectra in accord with the assigned structure.

(8) Prepared from 1,6-heptadiyn-4-ol (**3**) [M. Gaudemar, *Compt. Rend.*, **239**, 1303 (1954); *Ann. Chim.* (Paris), [1] **13**, 205 (1956)] and 2 molar equiv of ethylmagnesium bromide.

(9) See R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965).

(10) Sample placed on block just below this temperature.

(11) *Inter alia*, N. J. Leonard and C. W. Schimelpfenig, *J. Org. Chem.*, **23**, 1708 (1958).

The relative configuration of the two hydroxyl groups in **5a** was not determined.

Treatment of **5a** with excess methanesulfonyl chloride in pyridine at room temperature for 16 hr gave the dimethanesulfonate **5b** [75% yield; mp 205 dec;[10] $\lambda_{max}^{CH_3CN}$ 227 mμ (ε 1520), 240 (1140), and 254 (720)],[7] which was then boiled with potassium hydroxide in aqueous methanol and dimethyl sulfoxide for 1 hr. This reaction effected elimination and rearrangement[12] to give a mixture of products from which a tridehydro[26]annulene could be separated in *ca.* 2% yield by preparative thin layer chromatography on silica gel.[13] The positions of the three acetylenes or the stereochemistry of the double bonds in this compound cannot be assigned at present, and the 1,9,17-tridehydro structure **6** is one of many possibilities. The [26]annulene formed red-brown crystals (red in concentrated solution), decomposing on attempted melting point determination; mol wt 332.156[6] (calcd for $C_{26}H_{20}$, 332.156); λ_{max}^{ether} 237 mμ (ε 23,000), 291 (33,700), 300 (33,400), 383 (119,000),[14] and 451 (12,300); infrared bands (KBr) 2140 (w) (acetylene) and 988 (s) cm^{-1} (*trans* double bond), no allene band at *ca.* 1950 cm^{-1}. The monocyclic nature of the substance was established by catalytic hydrogenation in ethyl acetate over platinum, which led to cyclohexacosane (mol wt 364).[6]

The nmr spectrum of tridehydro[26]annulene at room temperature (100 Mc/sec, in $CDCl_3$ or CD_3COCD_3, TMS used as internal standard) exhibited a very broad multiplet at *ca.* 2.0–4.5, no discrete inner or outer protons being recognizable. Cooling to −60° caused essentially no change. The spectrum was similar to that of tridehydro[30]annulene[3b] and pentadehydro[30]annulene,[3b] as well as that of a long-chain linear polyene-polyyne.[16] It appears therefore that dehydroannulenes containing $(4n + 2)$ out-of-plane π electrons show no ring current and resemble a linear analog when $n \geqslant 6$. As regards lower members of this series, the five known dehydro[14]annulenes ($n = 3$) and the three known dehydro[18]annulenes ($n = 4$) have all been found to sustain a diamagnetic ring current.[3] It is now of interest to synthesize and study the behavior of members belonging to the unknown dehydro[22]annulene ($n = 5$) series.

Regarding dehydroannulenes containing $4n$ out-of-plane π electrons, the largest member to be investigated is tetrahydro[24]annulene ($n = 6$).[17] This substance was found to possess a paramagnetic ring current,[3b,18] as do the lower known members containing 12, 16, and 20 out-of-plane π electrons ($n = 3$, 4, and 5, respectively).[3b] It will be of interest to prepare and study the behavior of a dehydro[28]annulene, the next higher member of this series ($n = 7$), in order to find the limiting size for the existence of a paramagnetic ring current.

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(12) The base treatment under similar conditions of a cyclic compound containing the 1,6-heptadiyn-4-ol methanesulfonate grouping to give cyclic conjugated systems has been described by us previously (J. Mayer and F. Sondheimer, *J. Am. Chem. Soc.*, **88**, 602, 603 (1966)).

(13) The only other highly colored substance eluted [*ca.* 2% yield; red-brown powder; main λ_{max}^{ether} 390 mμ (ε 131,000)] showed mol wt 428.[6] The formula therefore appears to be $C_{27}H_{24}O_3S$ (calcd mol wt 428), derived from the dimethanesulfonate **5b** by elimination of *one* molecule of methanesulfonic acid. It is possible that this substance is the methanesulfonate of a monohydroxybisdehydro[26]annulene, but it has not been investigated further.

(14) By comparison, tetradehydro[24]annulene showed the principal $\lambda_{max}^{isooctane}$ 340 mμ (ε 225,000),[15a] and tridehydro[30]annulene showed the principal $\lambda_{max}^{isooctane}$ 397 mμ (ε 114,000).[15b]

(15) (a) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 260 (1962); (b) F. Sondheimer and Y. Gaoni, *ibid.*, **84**, 3520 (1962).

(16) W. H. Okamura and F. Sondheimer, unpublished observations.

(17) A hexadehydro[36]annulene ($n = 9$) has been obtained in impure form, but the nmr spectrum was not determined.[15a]

(18) See J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967); H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, in press.

(19) National Research Council (Canada) Postdoctoral Overseas Fellow, 1965–1967.

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On Triplet States of Flavins

Sir:

We have observed anaerobically the phosphorescence of riboflavin (RF) at 6650 A (uncorrected) in a 0.8% glucose–water matrix,[1] while others reported the emission at shorter wavelengths (6030–6100 A) under aerobic conditions and in an organic matrix.[2–4]

Recently, Steele and Cusachs[5] proposed the spin-conserved energy-transfer process given by eq 1 to account for the apparent oxygen requirement in the phosphorescence emission from RF. Ironically, oxygen is a rather well-known triplet quencher.[6]

$$O_2^{t} + RF^{s} \underset{h\nu(6030\ A)}{\overset{h\nu(4500\ A)}{\rightleftarrows}} O_2^{s*} + RF^{t} \qquad (1)$$

We investigated flavin triplets theoretically in an attempt to establish singlet–triplet intervals in RF. Reasonably reliable values for triplet states can be computed by means of the SCF–ASMO–CI method in the Pariser–Parr–Pople semiempirical framework.[7,8]

Several flavins were investigated. Methyl groups were treated by means of the group orbital and heteroatom approximations.[9] Different sets of semiempirical integrals were used and most of these were taken from published sources.[10] The assumed geometry of the basic isoalloxazine ring was the same as in ref 11.

Results are shown in Table I. Several conclusions can be made from the results presented. (1) The sets of integrals used by Grabe[11] gave triplet states of considerably low energies. The calculated singlet–singlet transition energies were also too low to compare favorably with the experimental absorption spectrum. Notice also that the first triplet is below the singlet ground state in the case of C. Therefore, we conclude that the results for A, B, and C are questionable due to the use of inappropriate integrals.

(2) Values obtained for D and E appear to be reasonable with respect to the bond-order matrix and singlet–

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(1) P. S. Song and D. E. Metzler, *Photochem. Photobiol.*, in press.

(2) R. H. Steele, *Biochemistry*, **2**, 529 (1963).

(3) J. M. Lhoste, A. Haug, and P. Hemmerich, *ibid.*, **5**, 3290 (1966).

(4) J. Posthuma and W. Berends, *Biochim. Biophys. Acta*, **122**, 422 (1966).

(5) R. H. Steele and L. C. Cusachs, *Nature*, **213**, 800 (1967).

(6) K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

(7) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

(8) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 131, and references therein.

(10) A complete list of semiempirical integrals used in methods A–R in Table I is available upon request. Some of the parameters are tabulated in P. S. Song and T. A. Moore, *J. Quantum Chem.*, in press.

(11) B. Grabe, *Biopolymers Symp.*, **1**, 283 (1964).