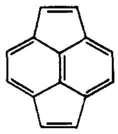
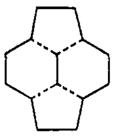
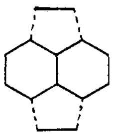
cross-link, introduced as described above, may exist with no alteration in the above conclusions.

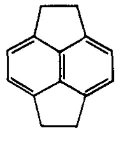
A particularly interesting pentalenoid system is pyracylene III which, in terms of the above discussion, can be treated as a cyclododecahexaene with a vinyl cross-link (IIIa). On the other extreme, a naphthalene core with two vinyl bridges (IIIb) is a reasonable model. To examine these possibilities, we began to explore the chemistry of pyracylenes.[4] We wish now to report the synthesis and spectral properties of the parent hydrocarbon.

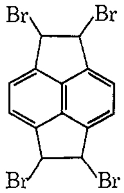

III

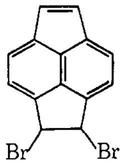

IIIa


IIIb

Controlled bromination of pyracene IV with 3.7 equiv of NBS for 15 min in refluxing CCl_4 produced a colorless tetrabromide, decomposing at 150°, whose spectral and analytical (*Anal.* Found: C, 34.06; H, 1.70; Br, 64.40) properties identify it as 1,2,5,6-tetrabromopyracene (V). The ultraviolet spectrum[5] showed maxima [λ (mμ) (log ε)] at 232 (4.68), 318 (4.08), and a shoulder at 332 (3.97). Its nmr spectrum[6a] showed only two singlets of equal intensity at 6.00 and 7.65 ppm fully confirming the assignment of the symmetrical tetrabromide. The mass spectrum[6b] showed no molecular ion peak. The highest and most intense peak in the spectrum appeared at m/e 176 and the second most intense peak appeared at $m/2e$ 88. These peaks correspond to the pyracylene molecular ion and its dication, respectively, and the spectrum corresponds to that of pyracylene. The fragmentation pattern is remarkably similar to that of acenaphthylene.


IV


V


VI

Debromination of V with iodide ion[4] in DMF, acetonitrile, or acetone proceeded smoothly to produce a solution of pyracylene III. This compound had an ultraviolet spectrum[5] very similar to that of dibromopyracylene[4]—maxima (in mμ) at 385, 378, 341, 332, and 220 with extensive tailing to 650 mμ. The nmr spectrum[6a] showed two singlets of equal intensity at 6.01 and 6.52 ppm. Hydrogenation of a deep red ethyl acetate solution of III utilizing platinum oxide produced a quantitative yield (based on V) of pyracene—fully confirming the structure. Attempts to isolate pyracylene in the solid state produced only amorphous yellow polymers.

The full ppm upfield shift of the proton in the nmr spectrum is inconsistent with any $4n + 2$ aromatic model (*e.g.*, IIIb). Recently, Pople and Untch[7] provided a theoretical basis for the presence of a paramagnetic ring current in $4n$ monocyclic systems. Nmr studies of the [16]-[8] and [24]annulenes[9] provided experimental verification. Although no satisfactory model for a [12]annulene such as is present in III exists,[10] it appears a similar explanation is required to explain the large shift. Thus, the periphery model best accounts for these properties.

An excellent correlation of the energy of the first unoccupied molecular orbital with half-wave potentials exists.[11] Such a correlation predicts a first half-wave potential of -0.924 ± 0.109 v for a system in which the electron enters a nonbonding level.[12] Triphenylmethyl radical, which is such a system, exhibits its first wave at -1.05 v *vs.* sce. Pyracylene shows two one-electron waves at -1.056 and -1.635 v *vs.* sce[13] in DMF, in excellent agreement with the theoretical prediction of the presence of a nonbonding level.

Following the debromination reaction by nmr revealed the presence of an intermediate which eventually is completely converted to pyracylene. The nmr in acetone[14] showed an AB pattern for four protons with H_A at 7.96 ppm and H_B at 7.66 ppm and $J_{AB} = 7.0$ cps, a singlet for two protons at 7.24 ppm, and a singlet for two protons at 6.12 ppm, in complete accord with structure VI. The presence of VI as a detectable intermediate suggests that proceeding to the fully unsaturated system does not produce a substantial increase in stability.

Acknowledgment. We express our gratitude to the National Institutes of Health, Grant No. GM-13587-01, and the Wisconsin Alumni Research Foundation for partial support of this work.

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[4] This paper forms part V in our series of studies in this area. For part IV see B. M. Trost and D. R. Brittelli, *Tetrahedron Letters*, 119 (1967); for part III see S. F. Nelsen, B. M. Trost, and D. H. Evans, *J. Am. Chem. Soc.*, **89**, 3034 (1967).

[5] Determined as a solution in ethanol.

[6] (a) Determined as a solution in CCl_4. (b) We are deeply indebted to Professors Lawrence A. Singer and Joseph Ciabattoni for this determination.

[7] J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966).

[8] G. Schroeder and J. F. M. Oth, *Tetrahedron Letters*, 4083 (1966).

[9] I. C. Calder and F. Sondheimer, *Chem. Commun.*, 904 (1966).

[10] Two models may be considered. *s*-Indacene exhibits absorptions at somewhat lower field than III (see K. Hafner, *Angew. Chem.*, **75**, 1041 (1963)). Cyclododecatrienetriyne shows an upfield shift of its protons in its nmr spectrum (see K. G. Untch and D. C. Wysocki, *J. Am. Chem. Soc.*, **88**, 2608 (1966), and F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966)).

[11] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 173–201.

[12] This predicted value is for aqueous dioxane; however, it has been shown that the first half-wave potential varies at most by only a few hundredths of a volt for changes from aqueous dioxane to anhydrous DMF. See ref 11 and P. H. Given, *J. Chem. Soc.*, 2684 (1958).

[13] We wish to thank Professor Dennis H. Evans for this determination.

[14] In these series of compounds, acetone causes a downfield shift of 0.1–0.2 ppm relative to carbon tetrachloride.

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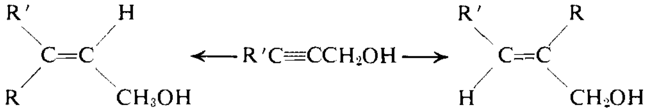
A New Stereospecific Synthesis of Trisubstituted Olefins. Stereospecific Synthesis of Farnesol

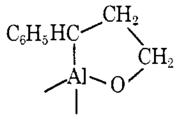
Sir:

This note describes a new synthetic method which allows the stereospecific conversion of propargylic alcohols to either 2-alkylated or 3-alkylated allylic alcohols (eq 1) and its application in the isoprenoid field.



(1)

Propargylic alcohols are converted by reaction with lithium aluminum hydride and subsequent hydrolysis into *trans*-hydrogenated allylic alcohols, in what is now a much used, standard synthetic process.[1] The reduction depends critically on the presence of the nearby hydroxyl group and in this respect is reminiscent of the reduction of allylic alcohols with lithium aluminum hydride, now known to involve organoaluminum intermediates (*e.g.*, I).[2] Our studies have been aimed at verifying the existence of intermediate vinylaluminum compounds in the reduction of propargylic alcohols by lithium aluminum hydride and at applying these intermediates to olefin synthesis by the stereospecific substitution of various groups for aluminum. The particular system chosen for study was the alcohol III, a potential precursor of farnesol, readily obtained from *trans*-geranylacetone by reaction with phosphorus pentachloride–2,6-lutidine in methylene chloride at 0° followed by dehydrochlorination of the resulting mixture of chlorides with sodium amide in liquid ammonia to form II[3] and hydroxymethylation with formaldehyde.[4] The mass spectrum of III revealed a molecular ion peak at 206.1664 (calcd 206.1671).

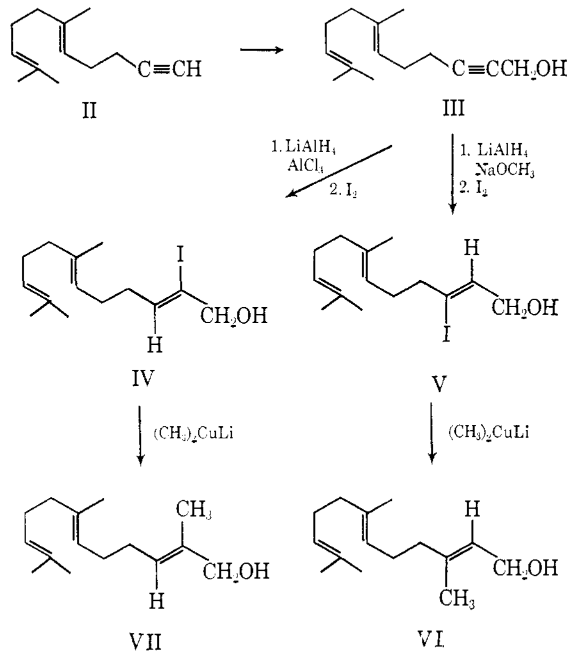


I

When the reduction of III was carried out with lithium aluminum hydride in tetrahydrofuran and the hydrolysis was performed with deuterium oxide (>99.5% D_2O), the product was monodeuterated allylic alcohol as expected for the intermediacy of a vinylaluminum derivative and, similarly, iodination of the hydride reduction mixture afforded monoiodinated allylic alcohol. Surprisingly, nmr analysis of the deuterated and iodinated reaction products indicated them to be mixtures in which the deuterium and iodine were attached not only γ but also β to the allylic hydroxyl. Further, the ratio of β:γ substitution product varied considerably from one reduction experiment to another and appeared to depend on the details of preparation of the hydride solution.

No attempt has been made to explain this unexpected variability, but instead a small number of modified hydride reagents were studied in an attempt to obtain greater selectivity and reproducibility. It was quickly discovered that the use of a solution of 0.1 *M* lithium aluminum hydride–aluminum chloride (mole ratio 60:1) in tetrahydrofuran at reflux for 3 hr led to the formation of an organoaluminum compound which produced the β-iodo alcohol IV exclusively upon iodination (excess I_2, −78°) and that a heterogeneous mixture of 0.1 *M* lithium aluminum hydride–sodium methoxide (mole ratio 1:2) in tetrahydrofuran at reflux for 3 hr led after iodination (excess I_2, −78°) specifically to the γ-iodo alcohol V. The yields of alcohols IV and V over both steps and after purification were in the range 60–75% with these reagents.

The reaction of the γ-iodo alcohol V with excess lithium dimethylcopper[5] at 0° for 63 hr (under nitrogen) afforded *trans,trans*-farnesol, identified by comparison with an authentic sample by nmr and infrared spectroscopy and vapor phase chromatography on Carbowax 20M and Epon resin columns.[6] Similar treatment of the β-iodo alcohol IV produced an isomer of farnesol having a methyl group β to the hydroxyl, 2,7,11-trimethyl-*trans,trans*-2,6,10-dodecatrien-1-ol (VII), as indicated by the appearance of a single unsplit peak in the nmr spectrum (in $CDCl_3$) at 4.15 ppm due to $-CH_2O$. The alcohol VII was shown by gas chromatography to be homogeneous under conditions which resolve it from *trans,trans*- and *trans,cis*-farnesols; the mass spectrum of VII revealed the molecular ion at *m/e* 222.1987 (calcd 222.1984), and the diphenylurethan derivative, mp 58.0–59.0°, afforded satisfactory analytical data.



By the same procedures used for the synthesis of the iodo alcohols IV and V from the propargylic alcohol III, 2-decyn-1-ol has been converted stereospecifically to 2-iodo-*trans*-2-decen-1-ol (reducing agent, $LiAlH_4$–$AlCl_3$, 60:1) and 3-iodo-*trans*-2-decen-1-ol (reducing agent, $LiAlH_4$–$NaOCH_3$, 1:2).

The methodology described herein is applicable to a wide variety of synthetic problems in which the stereospecific introduction of trisubstituted olefinic linkages is involved. Heretofore acetylenic precursors have been widely used for the stereospecific synthesis of *cis* or *trans* olefins of type XCH=CHY[1,7,8] and certain tri-

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(1) See R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworth and Co. (Publishers) Ltd., London, 1955, p 29.

(2) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948).

(3) For another preparation of II see P. A. Stadler, A. Nechvatal, A. J. Frey, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1373 (1957).

(4) F. Sondheimer, *J. Am. Chem. Soc.*, 74, 4040 (1952).

(5) E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967).

(6) The high-resolution mass spectrum of synthetic farnesol indicates a parent mass of 222.1985 (calcd 222.1984). The diphenylurethan derivative of synthetic farnesol had mp 60–61° [see R. B. Bates, D. M. Gale, and B. J. Gruner, *J. Org. Chem.*, **28**, 1086 (1963)], undepressed upon admixture with an authentic sample.

(7) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).

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)].

(10) This work was supported by Predoctoral Fellowships to J. A. K. (National Science Foundation) and G. H. P. (National Institutes of Health).

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Received June 12, 1967

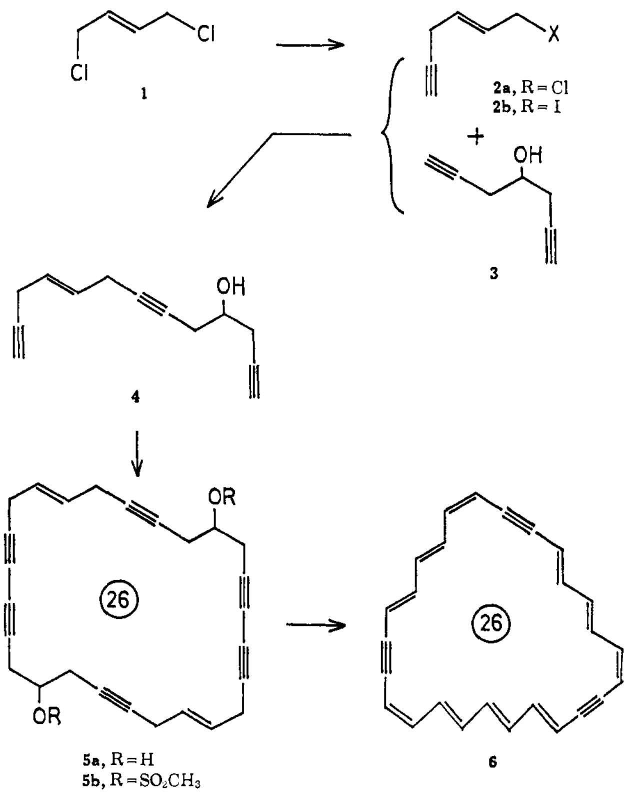
Tridehydro[26]annulene[1]

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).