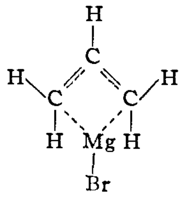
usual allyl compounds (see the spectrum of allylbenzene in Fig. 1), the substance gives an amazingly simple n.m.r. spectrum which, in fact, is of the general pattern expected for AX_4, where A and X are nuclei of spin $^1/_2$, having quite different chemical shifts, and all X's are equivalent with respect to A and each other.[2] The mutual interactions of such a system of nuclei result in a spectrum which can be described in terms of a single spin–spin coupling constant J_{AX} which in the present case has the value 12 ± 1 c.p.s. and leads to a symmetrical quintet of resonance lines for A and a doublet for the resonance of X.[3]

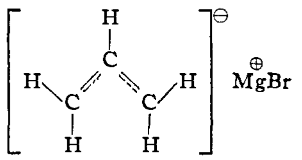
The n.m.r. spectrum of allylmagnesium bromide can be reasonably interpreted only if equilibrium (1) is assumed to be very rapid.[4]

$$\mathrm{BrMg{-}CH_2{-}CH{=}CH_2 \rightleftarrows CH_2{=}CH{-}CH_2{-}MgBr} \qquad (1)$$

To be sure, the merging of the separate resonances of the 1,3-protons of the allyl radical into an equivalent X_4 group could be taken to speak for the rapid equilibrium of eq. (1),[5] (2) a symmetrical bridged structure such as II[6] or the completely ionic structure III.



II



III

However, the fact that the 1,3-protons are in an X_4 group with no differentiation into *cis* and *trans* types requires that there be *rapid* rotation ($\gg$30 c.p.s.) around the C–C bonds of the allyl group. This would hardly be possible for II or III because of the considerable double-bond character expected for the C–C bonds of such entities. Thus, the only conclusion is that the two possible covalent forms of the Grignard reagent are in dynamic equilibrium (with $\tau \ll 0.01$ sec.) and the lifetime of each form is long enough to permit rotation around its 1,2 C–C bond.

Further n.m.r. studies of allylmagnesium bromide and other Grignard reagents are in progress.

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[2] *Cf.* H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

[3] *Cf.* J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chap. III.

[4] As far as is known at present, this equilibrium could be established by either inter- or intramolecular processes.

[5] *Cf.* Ref. 3, Chap. IV, for discussion and examples.

[6] W. G. Young and J. D. Roberts, THIS JOURNAL, **68**, 1472 (1946).

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RECEIVED FEBRUARY 26, 1959

2,6-DIAMINO-4-HYDROXYPTERIDINE, A NEW, NATURALLY OCCURRING PTERIDINE

Sir:

In hydrogenation experiments on 2-amino-4-hydroxypteridines, using platinum or palladium as catalysts, we noted the persistent occurrence of a greenish-yellow fluorescent compound in reoxidized samples submitted to paper chromatographic analysis. A 20% yield of the new compound was obtained by reduction of 2-amino-4-hydroxypteridine in dilute ammonia solution and reoxidation with manganese dioxide without exposure to air. The bright yellow compound was separated by paper chromatography (1-propanol–1% ammonia) from the other products of the reaction (starting material, and xanthopterin), and was obtained in pure form by eluting the appropriate band from the paper with aqueous ammonia and removing the ammonia. It was very insoluble in water but was readily soluble in dilute acid or alkali. Its elementary analysis indicated an empirical formula $C_6H_6N_6O$ (Calcd. for $C_6H_6N_6O$: C, 40.4; H, 3.37; N, 47.2. Found: C, 40.3; H, 3.12; N, 43.7). Its ultraviolet absorption spectrum had maxima in 0.1 N sodium hydroxide at 260 mμ ($E^{1\%}_{1\mathrm{cm.}}$, 1092), and 393 mμ ($E^{1\%}_{1\mathrm{cm.}}$, 345); maxima in 0.1 N hydrochloric acid were at 272 mμ ($E^{1\%}_{1\mathrm{cm.}}$, 883) and 377 mμ ($E^{1\%}_{1\mathrm{cm.}}$, 310). Some R_F values compared with those for xanthopterin (in brackets) are: 1-propanol, 1% ammonia, (2:1) 0.27 (0.23); 1-butanol, acetic acid, water (4:1:1), 0.26 (0.36); 4% sodium citrate, 0.37 (0.62). We have shown by these reactions that the compound is 2,6-diamino-4-hydroxypteridine: (1) Lumazine under the same conditions of reduction and reoxidation yields a different but very similar compound (presumably 2,4-dihydroxy-6-aminopteridine), indicating that the pyrimidine portion of the ring is unaltered. (2) 2-Amino-4-hydroxypteridine labelled in the 6 and 7 positions with C^{14} loses no radioactivity on conversion to the new compound, indicating that the pyrazine portion is unaffected. (3) The compound if again reduced with platinum in dilute sodium hydroxide solution and allowed to reoxidize in air yields a mixture of 2-amino-4-hydroxypteridine, xanthopterin and starting material. (4) On very gentle treatment with nitrous acid, the compound is almost quantitatively converted to xanthopterin, identified by paper chromatography and by ultraviolet and infrared spectra.

A variety of other pteridines including folic acid and biopterin yield 2,6-diamino-4-hydroxypteridine by the same process, along with xanthopterin and 2-amino-4-hydroxypteridine.

Considerable interest attaches to this compound not only because of the novel method of synthesis but also because we have been able to isolate it by paper chromatography from *Drosophila melanogaster* and from the blue-green algae, *Anacystis nidulans* and *Nostoc muscorum* G and identify it by paper chromatography and ultraviolet and infrared spectra. It is therefore probably widely distributed in nature. The functional significance of the 6-amino group, and the relationship of the compound to xanthopterin, folic acid and other naturally occurring pteridines remain to be elucidated. It is possible, for example, that 2,6-diamino-4-hydroxypteridine is an artifact arising from a very reactive compound (presumably 2-amino-4-hydroxy-5,8-dihydropteridine or 2-amino-4-hydroxy-7,8-dihydropteridine) by addition of ammonia during the isolation procedure.

Additions to the double bonds of the pteridine ring have been noted by Albert.[1] So far as we are aware, however, this is the first case in which a substituent has been added to the 6 position, presumably by addition to a double bond in the partially reduced ring, with subsequent further reoxidation.[2]

(1) A. Albert, "Current Trends in Heterocyclic Chemistry," A. Albert, G. M. Badger and C. W. Shoppee, eds., Academic Press, Inc., New York, N. Y., 1958, p. 20.

(2) This work was supported by the Rockefeller Foundation, the Robert A. Welch Foundation, Houston, Texas, and the National Science Foundation.

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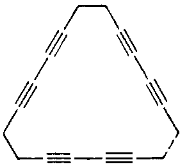
RECEIVED JANUARY 31, 1959

UNSATURATED MACROCYCLIC COMPOUNDS. VI. THE SYNTHESIS OF CYCLOÖCTADECA-1,3,7,9,13,15-HEXANE-5,11,17-TRIYNE, A COMPLETELY CONJUGATED EIGHTEEN-MEMBERED RING CYCLIC SYSTEM[1]

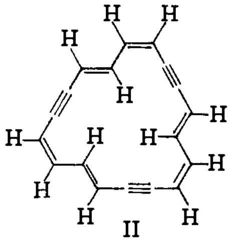
Sir:

It has been shown that the oxidative coupling of terminal diacetylenes may lead to large-ring polyacetylenes.[2,3] We have also found that certain linear 1,5-enynes $(-C{\equiv}C{-}CH_2CH_2{-}CH{=}CH{-})$ and 1,5-diynes $(-C{\equiv}C{-}CH_2CH_2{-}C{\equiv}C{-})$ undergo ready prototropic rearrangement on being treated with potassium *t*-butoxide in *t*-butyl alcohol, to yield, respectively, the corresponding conjugated trienes and dienynes.[4] A combination of these reactions appeared to provide a route to fully conjugated monocyclic large-ring systems and this objective has now been realized.

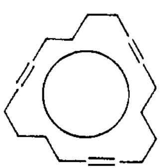
Cycloöctadeca-1,3,7,9,13,15-hexayne (I) (obtained in *ca.* 6% yield by the oxidation of 1,5-hexadiyne with cupric acetate in pyridine)[4] on treatment with potassium *t*-butoxide in *t*-butyl alcohol at 90° for 25 minutes rearranged in *ca.* 50% yield to a new substance, $C_{18}H_{12}$, which after chromatography on alumina crystallized from pentane as large brown plates, m.p. 190–192° (dec.; sample placed on block at 185°) (found: C, 94.71; H, 5.06). This substance is assigned the fully conjugated unstrained planar structure II [cycloöctadeca-1,7,13-(*cis*)-triene-3,9,15-(*trans*)-triene-5,11,17-triyne],[5] derived from I by prototropic rearrangement of each 1,5-diyne to a 1,3-dien-5-yne unit. This structure follows from its properties as well as from an alternative method of preparation.[6]



I



II



IIa

The ultraviolet spectrum in isoöctane showed maxima at 245, 254, 322, 334, 365, 385, 400 and 434 $m\mu$ (ϵ = 18,800, 14,700, 98,000, 160,000, 8,700, 11,700, 15,200 and 1,080) and in benzene at 329, 342, 391, 407 and 441 $m\mu$ (ϵ = 95,000, 155,000, 12,000, 15,200 and 1,100). The infrared spectrum (KBr) showed bands at 3.30(w), 4.63(w), 4.75(w), 7.06(w), 7.78(m), 8.19(w), 8.40(w), 9.06(w), 10.32 (s), 10.81(s), 11.86(s) and 13.20(s) μ. Hydrogenation in dioxane over platinum yielded cyclooctadecane, m.p. and mixed m.p. 72–73°, showing that no transannular reaction had occurred during the rearrangement.

The hexaene-triyne II contains a continuous molecular orbital and may be written as IIa.[7] It contains 18 π-electrons in conjugation and is the first conjugated monocyclic system known with more than the classical sextet. The substance complies with Hückel's rule for aromatic stability in cyclic molecular orbitals [presence of $(4n + 2)$ conjugated π-electrons],[8] although the carbon–carbon bonds are of course not all equivalent as would be required for maximum stability. As expected, II is a reasonably stable compound as judged by its method of formation in satisfactory yield, the exhibition of a melting point (with decomposition) near 200°, the fact that it can be kept with little change for several days at room temperature in light and air, etc.

In practice it was found most convenient to carry out the oxidation of 1,5-hexadiyne as before,[1] rearrange the total reaction product with potassium *t*-butoxide and chromatograph. In this way 0.41 g. of pure II was obtained simply from 15 g. of 1,5-hexadiyne. In addition other colored conjugated hydrocarbons were formed, the structures of which are being investigated.

We are grateful to Prof. R. B. Woodward and the late Prof. W. E. Moffitt for valuable discussions.

(1) Part V, see F. Sondheimer, Y. Amiel and R. Wolovsky, THIS JOURNAL, **79**, 4247 (1957).

(2) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **78**, 4178 (1956); **79**, 4247, 5817, 6263 (1957); *Proc. Chem. Soc.*, 22 (1957).

(3) G. Eglinton and A. R. Galbraith, *Chem. and Ind.*, 737 (1956); *Proc. Chem. Soc.*, 350 (1957).

(4) *Cf.* E. R. H. Jones, M. C. Whiting, *et al.*, *J. Chem. Soc.*, 3197, 3201, 3208, 3212 (1954).

(5) For a discussion, but not the realization, of syntheses of related cyclic planar conjugated vinylacetylenes, see T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

(6) F. Sondheimer, Y. Amiel and Y. Gaoni, THIS JOURNAL, **81**, 1771 (1959).

(7) *Cf.* W. von E. Doering and L. H. Knox, *ibid.*, **74**, 5683 (1952).

(8) E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

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RECEIVED FEBRUARY 13, 1959

UNSATURATED MACROCYCLIC COMPOUNDS. VII.[1] SYNTHESIS OF CYCLOÖCTADECA-1,3,7,9,13,15-HEXAENE-5,11,17-TRIYNE FROM 1,5-HEXADIYN-3-OL

Sir:

It has been shown recently that macrocyclic polyacetylenes can be prepared simply by the oxidative coupling of certain terminal diacetylenes.[2] A possible approach to the synthesis of completely conjugated macrocyclic unsaturated compounds involved the coupling of the hitherto unknown 1,5-hexadiyn-3-ol (I) and subjecting any

(1) Part VI, F. Sondheimer and R. Wolovsky, THIS JOURNAL, **81**, 1771 (1959).

(2) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **78**, 4178 (1956); **79**, 4247, 5817, 6263 (1957); G. Eglinton and A. R. Galbraith, *Chem. and Ind.*, 737 (1956); *Proc. Chem. Soc.*, 350 (1957).