Pasadena, Calif., who recorded the nmr spectra of some of the reaction mixtures.

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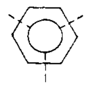
1,3,7,9,13,15-Hexadehydro[18]annulene[1]

Sir:

1,5,9-Tridehydro[12]annulene (**2**), first discussed in 1948 by Sworski,[2] has been synthesized recently by two groups.[3,4] This is a system containing 4*n* out-of-plane π electrons, formally derived from the (4*n* + 2) system benzene (**1**) by the insertion of three acetylene groupings at the places indicated. The nmr spectrum of **2** consists of a singlet at τ 5.58, and the comparatively high-field position appeared to provide experimental evidence for the existence of a paramagnetic ring current in 4*n* π-electron systems.[5] However, the possibility could not be excluded that the high-field position is due to the anisotropy of the triple bond.

We considered that information regarding this problem could be obtained by the preparation of 1,3,7,9,13,15-hexadehydro[18]annulene (**3**), formally derived from **1** by the insertion of three diacetylene groupings at the places indicated. The protons in this substance are in a similar environment to those in **2**, but **3** contains (4*n* + 2) out-of-plane π electrons, and it should therefore possess a diamagnetic ring current.[6] We now describe a synthesis of **3**,[7] the nmr spectrum of which provides strong evidence that the high-field position of the resonance of **2** is indeed due to a paramagnetic ring current.



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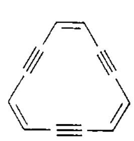

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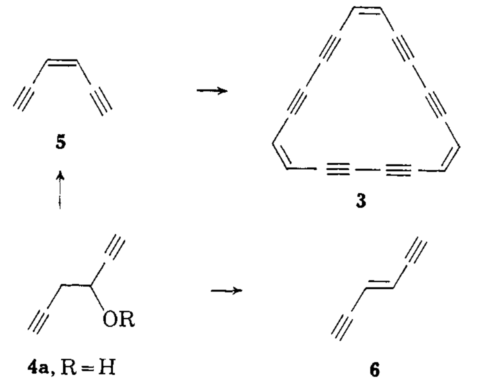

5

3

4a, R = H
b, R = Ts

6

Reaction of hexa-1,5-diyn-3-ol (**4a**)[8] with *p*-toluenesulfonyl chloride (1.1 molar equiv) and pyridine (1.5 molar equiv) yielded 80% of the *p*-toluenesulfonate **4b**, mp 74.5–75.0°. Treatment of **4b** with excess 1,5-diazabicyclo[4.3.0]non-5-ene[9] in ether at room temperature for 1 hr[10] gave rise to 70% of a mixture containing *ca.* 40% of *cis*-hex-3-ene-1,5-diyne (**5**) and *ca.* 60% of *trans*-hex-3-ene-1,5-diyne (**6**),[11] separated by preparative glpc. The *cis* isomer **5** (>99% pure by glpc) was a liquid showing $\lambda_{\max}^{\mathrm{MeOH}}$ 250 mμ (ϵ 14,500) and 262 mμ (ϵ 12,500); $\nu_{\max}^{\mathrm{film}}$ (cm^{-1}) 3295 (s) ($HC\equiv$), 2105 (w), 2085 (w) ($C\equiv C$), and 752 (m), 723 (m) (*cis*-$CH=CH$), only very weak band (at 940) in 1000–900 region; nmr spectrum (CCl_4, 100 Mcps), 2 H singlet at τ 4.11 (olefinic protons) and 2 H singlet at τ 6.72 (acetylenic protons). The *trans* isomer **6** (>99% pure by glpc) was a liquid showing $\lambda_{\max}^{\mathrm{MeOH}}$ 251 mμ (ϵ 20,400) and 263 mμ (ϵ 18,100); $\nu_{\max}^{\mathrm{film}}$ (cm^{-1}) 3300 (s) ($HC\equiv$), 2115 (w), 2090 (w) ($C\equiv C$), and 941 (m) (*trans*-$CH=CH$), no band in 800–700 region; nmr spectrum (CCl_4, 100 Mcps), 2 H singlet at τ 3.99 (olefinic protons) and 2 H singlet at τ 6.94 (acetylenic protons).

The crude mixture of **5** and **6** (from 1 part **4b**) was oxidized with cupric acetate monohydrate (15 parts) in pyridine (100 parts) at room temperature for 2 hr. This reaction led to a mixture of products, from which the cyclic "trimer" **3** could be separated in 3.1% yield (based on **4b**) by chromatography on alumina.[12] Substance **3** formed amber prisms (yellow in concentrated solution), which turned black at *ca.* 75° and then exploded at *ca.* 85° on attempted melting point determination (capillary); $\lambda_{\max}^{\mathrm{cyclohexane}}$ 227 mμ (ϵ 25,500), 236 (21,500), 260 (5900), 315 sh (41,000), 317 (41,500), 333 (75,800), 357 (13,000), 366 (7400), 378 (15,500), 388 (17,600) and 405 sh (790); $\nu_{\max}^{\mathrm{KBr}}$ 2180 (w) cm^{-1} and 2110 (w) cm^{-1} ($C\equiv C$); mass spectrum, molecular ion *m/e* 222.047 (base peak) (calculated for $^{12}C_{18}H_6$, 222.047). *Anal.* Calcd for $C_{18}H_6$: C, 97.28, H, 2.72. Found: C, 97.29; H, 2.76. The crystalline substance decomposed within a few hours at room temperature but was relatively stable in dilute ether solution. The monocyclic nature of **3** was confirmed by catalytic hydrogenation in ethanol over platinum oxide, which led to cyclo-

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(1) Part LIII in the series "Unsaturated Macrocyclic Compounds." For part LII, see R. H. Mitchell and F. Sondheimer, *Tetrahedron*, in press.

(2) T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

(3) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965); F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966).

(4) K. G. Untch and D. C. Wysocki, *ibid.*, **88**, 2608 (1966).

(5) J. A. Pople and K. G. Untch, *ibid.*, **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, p 109.

(6) See F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967); 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, p 75.

(7) A previous attempt to prepare **3** was unsuccessful.[8] For the synthesis of other dehydro[18]annulenes, see F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 260 (1962); R. Wolovsky, *ibid.*, **87**, 3638 (1965).

(8) F. Sondheimer, Y. Amiel, and Y. Gaoni, *ibid.*, **84**, 270 (1962).

(9) H. Oediger, H. J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

(10) For the base elimination of *p*-toluenesulfonates of β-hydroxyacetylenes to a mixture of conjugated *cis*- and *trans*-vinylacetylenes, see G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950); J. L. H. Allan and M. C. Whiting, *ibid.*, 3314 (1953).

(11) See A. Roedig and K. Kiepert, *Ann.*, **593**, 55, 71 (1955); G. Peiffer, *Bull. Soc. Chim. France*, 537 (1963); T. Böhm-Gössl, W. Hunsmann, L. Rohrschneider, W. M. Schneider, and W. Ziegenbein, *Chem. Ber.*, **96**, 2504 (1963).

(12) In separate cupric acetate oxidation experiments, *trans*-hex-3-ene-1,5-diyne (**6**) was found to give no **3**, while the *cis* isomer **5** produced **3** in *ca.* 20% yield. Similarly, hexa-1,5-diyne on oxidation with cupric acetate in pyridine has been shown to yield the corresponding cyclic trimer, in addition to higher cyclic oligomers.[7] By contrast, the ring compounds *o*-diethynylbenzene and 1,2-diethynylcyclohexene under these conditions gave the corresponding cyclic dimers, but none of the cyclic trimers: O. M. Behr, G. Eglinton, A. R. Galbraith, and R. A. Raphael, *J. Chem. Soc.*, 3614 (1960); G. M. Pilling and F. Sondheimer, unpublished experiments.

octadecane (mass spectrum, molecular ion m/e 252).

The nmr spectrum of **3** (CCl$_4$, 100 Mcps) consisted of a singlet at τ 2.98. Compared with the *cis*-enediyne **5** (τ 4.11) as a model, the downfield shift in the $(4n + 2)$ π-electron system **3** is therefore τ 1.13, and the upfield shift in the $4n$ system **2** is τ 1.47. This provides strong evidence for the existence of a diamagnetic ring current in **3** and a paramagnetic ring current in **2**.[13]

Acknowledgment. We are indebted to Professor Dr. O. Bayer and Dr. H. Oediger, Farbenfabrik Bayer, Leverkusen, for a generous gift of 1,5-diazabicyclo-[4.3.0]non-5-ene.

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(13) The results appear not to be in accord with the ideas of J. I. Musher, *J. Chem. Phys.*, **43**, 4081 1965; **46**, 1219 (1967); *Advan. Magnetic Resonance*, **2**, 177 (1966).

(14) Supported by the Air Force Office of Scientific Research and the National Academy of Sciences, National Research Council.

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Beam Studies of Energy Dependence of Hot-Atom Reactions

Sir:

The reactions of neutral species above threshold have been explored using nuclear recoil[1] and photochemical techniques.[2] These methods, while uncovering the richness of the field, can only provide limited data on the energy dependences of hot processes. We report here on beam experiments aimed toward providing such information on reactions of hot tritium.[3]

The apparatus ADAM was used to generate beams of monoenergetic tritium ions in the energy range 1–200 ev (Figure 1). Bombardment with 150-ev electrons was used to produce T_2^+ from T_2 gas and T^+ from T_2 which had been dissociated in a tungsten oven at 2500°K. The ions were extracted, accelerated to 200 ev, focused by a series of electrostatic lenses, and mass-analyzed by a simple Wien filter. After deceleration to the desired energy by a 12-element exponential lens, the beam was monitored by passing through a grid intercepting a known fraction of the current. Finally, it impinged on a liquid-nitrogen-chilled target of a solid hydrocarbon, cyclohexane being used as a prototype. The target surface was continually renewed by deposition of fresh material. Positive charge build-up was prevented by electrons from a filament near and slightly negative with respect to the target.

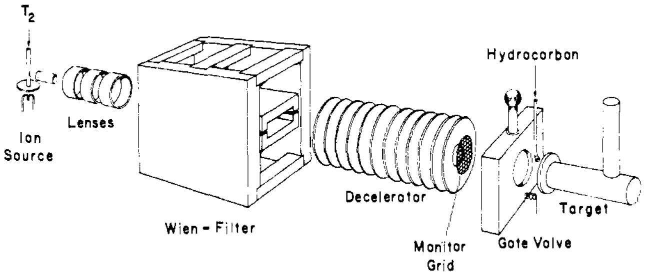

Figure 1. Schematic representation of ADAM apparatus.

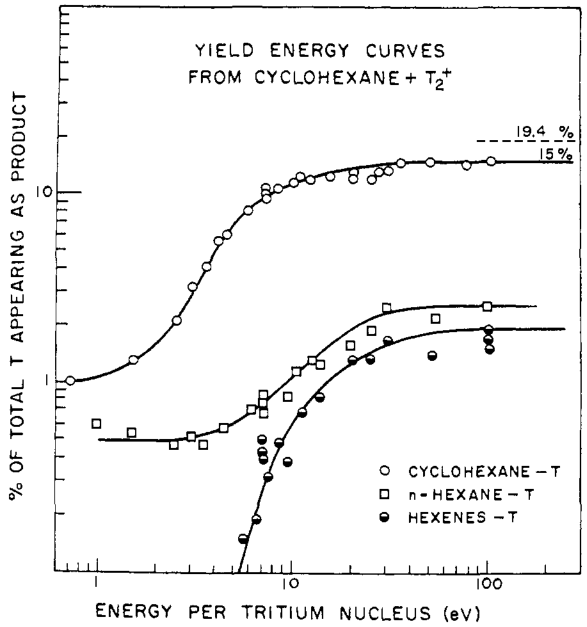

Figure 2. Log–log plot of yields of labeled products from T_2^+ beam interacting with solid cyclohexane. Yield of cyclohexane-t from recoil tritium is indicated by dashed line.

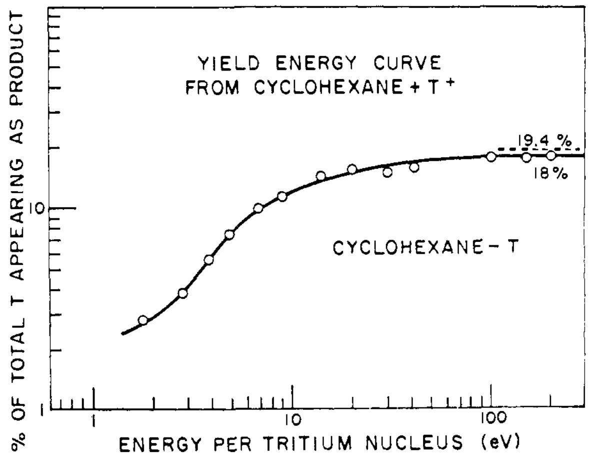

Figure 3. Log–log plot of yields of labeled cyclohexane-t from T^+ beam interacting with solid cyclohexane. Yield from recoil tritium is indicated by dashed line.

At the end of a run, the target was volatilized and analyzed for tritiated products by radio gas chromatography.[1,4] Absolute yields of cyclohexane-t and other products are shown in Figures 2 and 3 as a function of kinetic energy per T atom. Cyclohexane-t yields obtained in separate experiments with recoil tritium and solid cyclohexane[5] are also indicated.

Other studies have shown that the dominant reaction of hydrogen ions with hydrocarbons is charge transfer, proceeding with large cross section.[6,7] This process,

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(1) R. Wolfgang, *Ann. Rev. Phys. Chem.*, **16**, 15 (1965).

(2) (a) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 2999, 3007 (1964); (b) A. Kuppermann and J. M. White, *ibid.*, **44**, 4352 (1966); (c) C. C. Chou and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 2612 (1966).

(3) The first work on low-energy tritium beams was carried out by J. M. Paulus and J. P. Adloff (*Radiochim. Acta*, **4**, 146 (1965); J. M. Paulus, Thesis, Université de Strasbourg, 1966) using T^+ interacting with butane gas. A variety of processes presumably including hot-atom, ion–molecule, and surface interactions appear to be involved in this system, and the authors do not offer a definitive interpretation of their results.

(4) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, 30, 903 (1958).

(5) The technique used to obtain absolute yields from recoil tritium interacting with solids will be discussed elsewhere.

(6) W. A. Chupka and E. Lindholm, *Arkiv Fysik*, **25**, 349 (1963).

(7) J. Futrell, F. P. Abramson, and T. O. Tiernan, private communication.