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4,5 : 8,9-DIBENZO-2,10-CYCLOUNDECADIEN-6-YNE: A POTENTIAL PRECURSOR OF A NON-BRIDGED [11]ANNULENYL CATION

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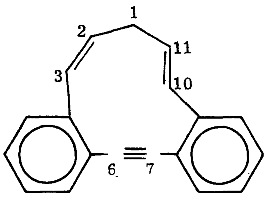
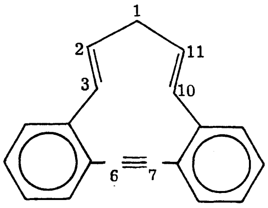
Two geometrical isomers of 4,5 : 8,9-dibenzo-2,10-cycloundecadien-6-yne were prepared by a Wittig reaction between 2,2'-diformyldiphenylacetylene and trimethylenedi(triphenylphosphonium bromide). Their stereochemical configuration, cis, trans (I) and trans, trans (II) were deduced from the nmr spectral data. Attempts to use (I) and (II) as precursors to the [11]annulenyl cation (III) have so far not been realized.

Bridged cycloundecapentaenes have previously been prepared by Vogel and Ogawa. These neutral parent hydrocarbons served as precursors of carbenium ions which manifest aromatic character.[1-4] Somewhat surprisingly, bridged hetero[11]annulenes do not possess paratropic character and behave like simple cyclic olefins.[5] We report the preparation and properties of cis,trans-4,5 : 8,9-dibenzo-2,10-cycloundecadien-6-yne (I) and trans,trans-4,5 : 8,9-dibenzo-2,10-cycloundecadien-6-yne (II). These two geometrical isomers may serve as precursors to the non-bridged [11]annulenyl cation (III).[6]

A Wittig reaction between 2,2'-diformyldiphenylacetylene[7] and trimethylenedi(triphenylphosphonium bromide)[8] with sodium methoxide in DMF at high dilution at 70°C (1 hr.) and 80°C (6 hrs.) afforded a mixture of (I) and (II). Chromatography on silica gel, gave (I) as the major product[9]



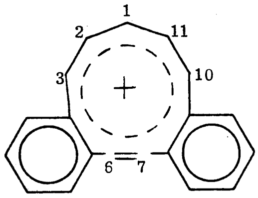
I



II

(2-3% yield of an oily substance, 10% yield from consumed 2,2'-diformyldiphenylacetylene). The structure of (I) was deduced from its spectral properties as follows: mass spect. m/e = 243 (M^+ +1, 14%), 242 (M^+, 70%), 241 (M^+ -1, 100% parent peak), 121 (M^{++}, 7%); ir (neat) 3060, 3000, 2926, 2860, 1460, 1430, 960 (trans double bond), 790 and 750 cm^{-1}; uv, $\lambda_{max}^{CH_3CN}$ 253 (ϵ 110,000), 259^s (106,000), 293 (12,400), 317 nm (12,700). The nmr spectrum[10] of (I), consists of methylene protons absorption, olefinic protons absorption and an aromatic multiplet. The methylene protons (the X part of an ABX_2 pattern) appeared as eight lines centered at 2.74 ppm (2H, $J_{1,2}$ = 8.0 Hz, $J_{1,11}$ = 6.0 Hz, $J_{1,10}$ = 1.0 Hz, $J_{1,3} \leq$ 0.5 Hz), assigned to H_1. In the olefinic region two AB parts of two ABX_2 spin systems appeared. One AB part appeared as triplets and had the following parameters: δ_A = 6.13 ppm (1H, assigned to H_{11}, $J_{10,11}$ = 16.0 Hz, $J_{1,11}$ = 6.0 Hz); δ_B = 6.47 ppm (1 H, assigned to H_{10}, $J_{10,11}$ = 16.0 Hz, $J_{1,10}$ = 1.0 Hz). The second AB spectrum had the following parameters: δ_A = 6.24 ppm (1 H, assigned to H_2, $J_{2,3}$ = 12.0 Hz, $J_{1,2}$ = 8.0 Hz; δ_B = 6.49 ppm (1H, assigned to H_3, $J_{2,3}$ = 12.0 Hz, $J_{1,3} \leq$ 0.5 Hz). On the basis of the value of $J_{2,3}$ and $J_{10,11}$, a cis and a trans configuration is ascribed to $C_2 = C_3$ and $C_{10} = C_{11}$ respectively. The aromatic protons appeared at δ = 7.11-7.58 ppm (8H, m). Double resonance experiments confirmed the above assignments. Irradiation at 2.74 ppm rendered the two double triplets at 6.13 and 6.24 ppm (H_{11} and H_2) into two normal A parts of an AB spectrum. Concomitantly, the narrow triplets at 6.47 and 6.49 ppm (H_{10} and H_3) turned into two normal B parts of an AB spectrum. Thus, the double resonance experiment gave two clear AB patterns. The nmr spectrum of (II)[9,10] consists of methylene protons absorption, olefinic protons absorption and an aromatic multiplet. It is much simpler than the spectrum of (I), and consists of one ABX_2 system. The methylene protons (the X spins of the ABX_2 spin system) appear as a triplet of triplets δ = 2.95 ppm (2H, $J_{1,2}$ = $J_{1,11}$ = 6.5 Hz, $J_{1,3}$ = $J_{1,10}$ = 1.0 Hz) assigned to H_1. The AB part of the ABX_2 appears as two triplets and two broad lines. It had the following parameters: δ_A = 6.10 ppm (2H, assigned to H_2 and H_{11}, $J_{2,3}$ = $J_{10,11}$ = 16.0 Hz, $J_{1,2}$ = $J_{1,11}$ = 6.5 Hz); δ_B = 6.81 ppm (2H, assigned to H_3 and H_{10}, $J_{2,3}$ = = $J_{10,11}$ = 16.0 Hz, $J_{1,3}$ could not be observed since this absorption appeared as two broad lines). The aromatic protons appeared at δ = 7.11-7.58 ppm (8H, m). Irradiation at 6.10 ppm rendered the triplet of triplets into a broad singlet. Irradiation at 2.95 ppm rendered the olefinic spectrum into an AB type spectrum. The two triplets at 6.10 ppm gave two sharp lines, while the broad lines at 6.81 ppm became narrower. On the basis of the value of $J_{2,3}$ = $J_{10,11}$ = 16.0 Hz a trans,trans configuration is ascribed to $C_2 = C_3$ and $C_{10} = C_{11}$. The nmr spectra of both (I) and (II) did not change in the temperature range of -60 to +100°C.

Attempts to convert the cycloundecadienyne system into the [11]annulenyl cation (III) were carried out under different experimental conditions and a variety of reagents. With triphenylcarbenium tetrafluoroborate in CD_3CN the disappearance of the olefinic and methylene absorptions in the nmr followed by the development of a triphenylmethane band at 5.56 ppm were noted. However no characteristic nmr spectrum of the ion could be observed. Experiments at lower temperature or with low nucleophilicity reagents (e.g. SbF_5) and superacids (e.g. magic acid) failed to give conclusive evidence, thus only a tentative formula of (III) may be assumed.



III

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References

1. a. P. Skrabal, in "MTP International Review of Science, Organic Chemistry, Series 1, Vol. 3, Aromatic Chemistry", pp. 237, Butterworths, London (1973).
   b. F. Sondheimer, Pure and Appl. Chem., 28, 331 (1971).
   c. P. J. Garratt, "Aromaticity", McGraw-Hill, London (1971).
   d. P. J. Garratt and M. V. Sargent, in Nonbenzenoid Aromatics, J. P. Snyder Editor, Academic Press, pp. 208. New York (1971).
2. W. Grimme, H. Hoffmann, and E. Vogel, Angew. Chem., 77, 348 (1965). See also: "Aromaticity" Special publication No. 21, The Chemical Society, London (1967).
3. a. H. Ogawa and N. Shimojo, Tetrahedron Lett., 4129 (1972).
   b. H. Ogawa and M. Kubo, Tetrahedron, 29, 809 (1973).
   c. M. Ogawa, N. Shimojo, and H. Kato, Tetrahedron, 29, 533 (1973).
   d. H. Ogawa, H. Kato, and M. Yoshida, Tetrahedron Lett., 1793 (1971).

4. J. Mayer and F. Sondheimer, J. Amer. Chem. Soc., 88, 602 (1966).
5. E. Vogel, R. Feldman, H. Duwell, H. D. Cremer, and H. Gunther, Angew. Chem., 84, 207 (1972).
6. An eleven-membered ring system which cannot form a conjugated carbocation has been reported by R. H. Mitchell and F. Sondheimer, Tetrahedron Lett., 2873 (1968).
7. H. W. Whitlock and J. K. Reed, J. Org. Chem., 34, 874 (1969).
8. G. Wittig, H. Eggers, and P. Duffner, Ann., 619, 10 (1958).
9. All compounds gave satisfactory elementary analyses. Usually (I) was obtained in > 95% purity. Isomer (II) always contained certain amounts of isomer (I).
10. Nmr spectra were recorded with the aid of a Varian HA100D spectrometer at 100 MHz, with TMS as internal reference. The decoupling experiments were carried out with the aid of a Hewlett-Packard 4204A oscillator.

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