CHEMISTRY LETTERS, pp: 307-310, 1974. Published by the Chemical Society of Japan

INTRAMOLECULAR RING CLOSURE OF 1,2,3,4-TETRACHLORO-6-(AZULEN-1-YL)FULVENE. FORMATION OF A CYCLOHEPT[cd]-s-INDACENE DERIVATIVE

Ichiro MURATA, Kagetoshi YAMAMOTO, and Mitsuhisa TAMURA

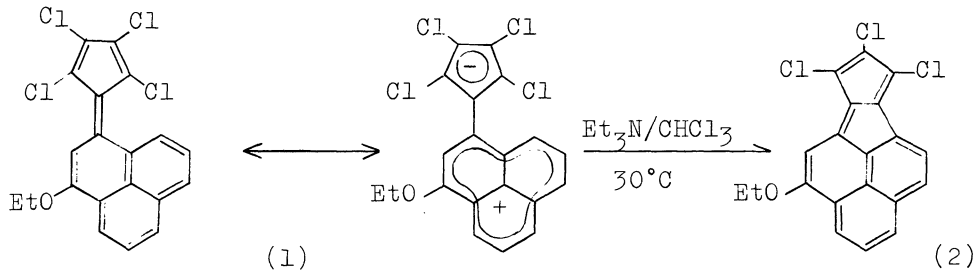
Department of Chemistry, Faculty of Science, Osaka University,

Toyonaka, Osaka 560

8,9,10-Trichlorocyclohept[cd]-s-indacene (4), a novel tetracyclic conjugated pi-electron system, has been synthesized by employing an intramolecular ring closure of 1,2,3,4-tetrachloro-6-(azulen-1-yl)-fulvene (3). Both the nmr data of 4 and SCF-MO calculation for the carbon skeleton of 4 have suggested that a polar structure (4a), such as sesquifulvalene, is a main contributor to the ground state of 4.

RECENTLY, we reported[1] that 2-ethoxy-9,10,11,12-tetrachloropentaphenafulvalene (1) reacted smoothly with triethylamine in chloroform at 30°C to produce 6,7,8-trichloro-4-ethoxypentaleno[1,2,3-cd]phenalene (2), containing a novel pentacyclic conjugated framework[2] [Scheme 1]. The observed solvent dependence of this ring closure reaction, half-lives in acetone and in n-pentane were found to 45 min and >10 hr, respectively, led us to propose the ionic reaction for this transformation. If such an ionic species is indeed involved, then one might expect that similar intramolecular ring formation would proceed in alternate molecule which has an electronically polar ground-state and a sterically favorable structure.

[Scheme 1]



(1) (2)

For an initial test of this hypothesis, the synthesis of the hitherto unknown ring system, cyclohept[cd]-s-indacene which is regarded as an isomer of cyclopenta-[a]phenalene,[3] was attempted. The calculated pi-electron charge density distributions in 6-(azulen-1-yl)fulvene revealed by simple HMO method are shown in Fig. 1. It is apparent that the highest charge density was found at C-1 and the substantially low charge densities were located at C-2' and C-8'. Furthermore, both the posi-

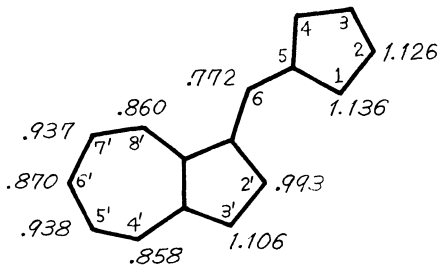


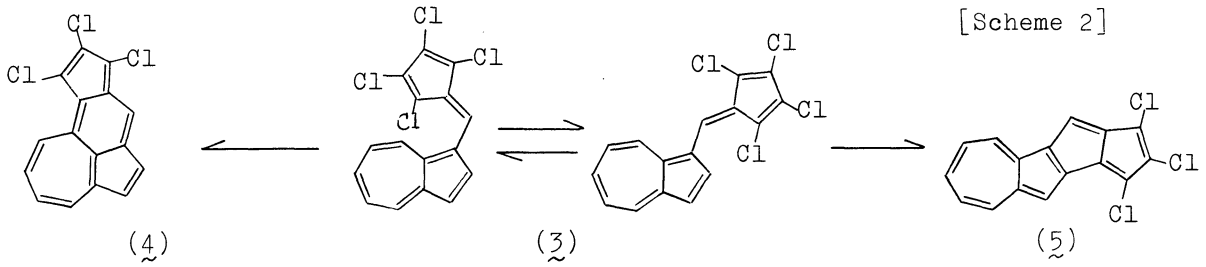
Fig.1. Calcd. charge density of 6-(azulen-1-yl)-fulvene by HMO.

tions, C-2' and C-8', are adequately situated for the intramolecular reaction in view of the free rotation about the bond connected between fulvene and azulene segments. Thus, intramolecular attack of C-1 to either C-2' or C-8' may be anticipated from the aforementioned stereoelectronic considerations.

Starting material for our synthesis, 1,2,3,4-tetrachloro-6-(azulen-1-yl)fulvene (3),[4] was readily available from the reaction of 1-formylazulene with tetrachlorocyclopentadiene in refluxing methanol, brown needles of mp >300°C, λ_{max}(cyclohexane) 272 (4.23), 337 (4.13) and 471 nm (log ε 4.63); δ^{TMS} (THF-d_8) 8.83 (d, H-2', $J_{2',3'}$=4.5 Hz), 7.66 (d, H-3', $J_{2',3'}$=4.5 Hz), 8.94 (d, H-4', $J_{4',5'}$=9.5 Hz), 7.60-8.15 (m, H-5', 6',7'), 8.67 (d, H-8', $J_{8',7'}$= 9.5 Hz) and 8.39 ppm (s, H-6).

A solution of 3 (50 mg) in anhydrous pyridine (250 ml) was heated under nitrogen atmosphere at 60°C, and the visible spectrum of the solution was measured in order to follow the progress of the reaction. The intensity of the absorption maximum of 3 near 490 nm gradually decreased and a new maximum appeared at 453 nm. When the absorbancy ratio at 490 and 453 nm reached a value of ca. 1.0 after 10 hr,[6] the pyridine solution was evaporated under reduced pressure at below 40°C to one-third the original volume, then poured into water and extracted with benzene. The benzene layer was washed thoroughly with water, dried over sodium sulfate and evaporated. Repeated silica gel (deactivated with 10% of water) column chromatography (light pet. ether, bp 30-50°C, was used as eluting solvent)[7] of the combined residue obtained from four such runs afforded two kinds of greenish black crystals, (4) and (5), in 4% and 7% yield, respectively [Scheme 2]. The assignment of the cyclohept-

[Scheme 2]



(4) (3) (5)

[cd]-s-indacene structure to 4 rests upon the following evidences. Exact mass measurement[8] of 4, 303.9614 (M^+, 100%, calcd. for $C_{16}H_7Cl_3$, 303.9613), 305.9589 (M+2, 96%, calcd, 305.9583), and 307.9539 (M+4, 32%, calcd, 307.9554) shows it to be a tetracyclic structure corresponding to the loss of hydrogen chloride from 3. The intense greenish brown color of a solution of 4 is due to a broad but intense visible band which has maxima of 397, 418, 453 (most intense), 580, and 608 nm with long tailing extending to 700 nm.[9] Compound 4 is unstable at ambient temperature in a concentrated solution for nmr measurement. The observed change of the proton resonance signals is shown in Fig. 2. The spectra in Fig. 2 clearly demonstrate

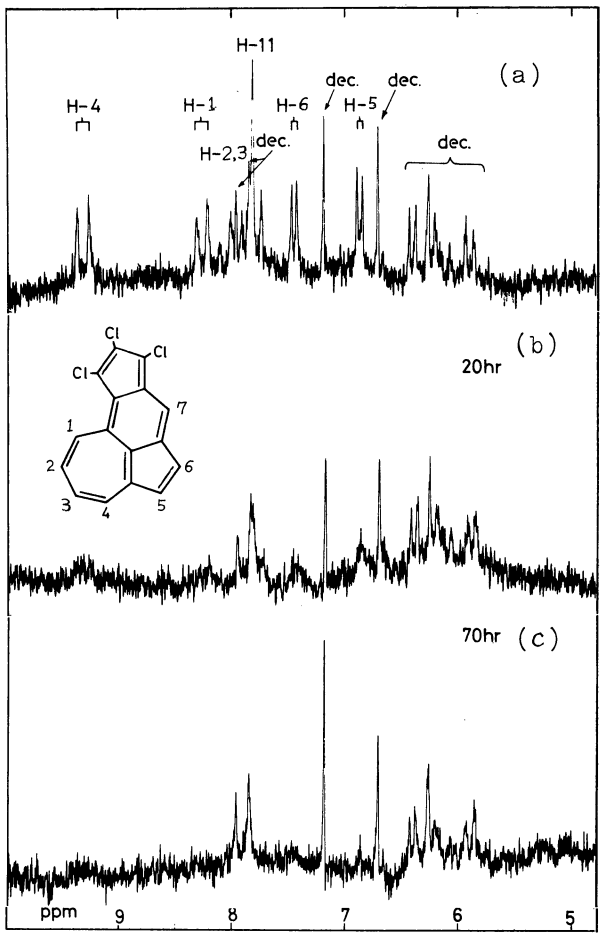


Fig. 2. 100 MHz nmr spectrum of 4.

the progress of decomposition of 4 even immediately after dissolution of 4, and during 70 hr the signals of 4 were completely replaced by those of decomposition product. Fortunately, the proton signals due to the unchanged 4 could readily be assigned by subtraction of the signals of Fig. 2c from those of Fig. 2a. The absorptions thus obtained, δ 6.90 (d, 1H, H-5, $J_{5,6}$=4.2 Hz),[10] 7.48 (d, 1H, H-6, $J_{6,5}$=4.2 Hz),[10] 7.77-8.14 (m, 2H, H-2,3), 7.82 (s, 1H, H-7), 8.30 (d, 1H, H-1, $J_{1,2}$= 10.0 Hz) and 9.35 (d, 1H, H-4, $J_{4,3}$=10.0 Hz), are consistent with the proposed structure.

Pi-electron charge densities and bond lengths of the carbon skeleton of 4 deduced from semi-empirical variable β SCF LCAO π-MO calculation[11] are summarized in Fig. 3. This result suggests that the polar resonance structure (4a) such as sesquifulvalene would make a large contribution to the ground-state of this molecule. Observed nmr spectrum is in accord with the above theoretical prediction. The absorptions for the seven-membered ring protons are found remarkably in low field owing to the deshielding effect of the positive charge developed on these carbon atoms.

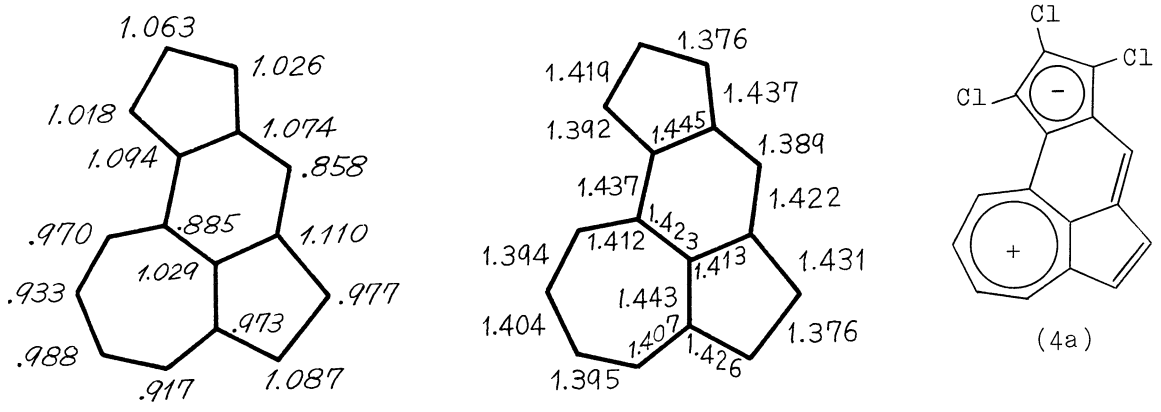


Fig. 3. Calcd. charge density (left) and bond order (Å) (right) for cyclohept[cd]-s-indacene by SCF-MO.

Although the structure of the alternate product has not been fully established due to its pronounced lability, the pentaleno[2,1-a]azulene structure (5) is tentatively assigned on the basis of the molecular weight determination by mass, m/e 304 (M^+, 100%), 306 (M+2, 100%), 308 (M+4, 46%), and the long wavelength absorptions at 410, 431, 464 and 593 nm.[8] This substance presumably results from the formation of the carbon-carbon bond between C-1 and C-2' of 3 and expulsion of hydrogen chloride. The structural elucidation of 5, of course, must await further studies.

REFERENCES AND NOTES

1) I. Murata, M. Okazaki, and T. Nakazawa, Angew. Chem., 83, 623 (1971); Angew. Chem. internat. Edit., 10, 576 (1971).
2) I. Murata, T. Nakazawa, and M. Okazaki, Tetrahedron Lett., 3269 (1970).
3) I. M. Aitken and D. H. Reid, J. Chem. Soc., 1956, 3487.
4) For the other 6-(azulen-1-yl)fulvenes, see K. Hafner and C. Bernhard, Ann. Chem., 625, 108 (1959); T. Toda, P. W. Yang, and T. Mukai, Sci. Repts. Tohoku Univ. Ser. I, 50, 208 (1967).
5) W. Treibs, J. J. Neupert, and J. Hiebsh, Chem. Ber., 92, 141 (1959).
6) Either higher reaction temperature or longer reaction time resulted in the marked decrease of the yields of 4 and 5.
7) A fair amount of products were decomposed in the course of chromatographic separation.
8) We are indebted to Mr. Y. Kato of Naka Work, Hitachi Ltd. for the exact mass measurement.
9) Intensities of the absorption maxima could not be obtained due to the instability of compound.
10) The assignment of signals at δ 6.90 and δ 7.48 to H-5 and H-6, respectively, was based solely on the charge densities.
11) We are indebted to Professor T. Nakajima of Tohoku University for the SCF-MO calculation.

(Received December 28, 1973)