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A NOVEL REACTION PRODUCT OF BENZO[d]TROPONE WITH 1,2,3,4-TETRACHLOROCYCLOPENTADIENE

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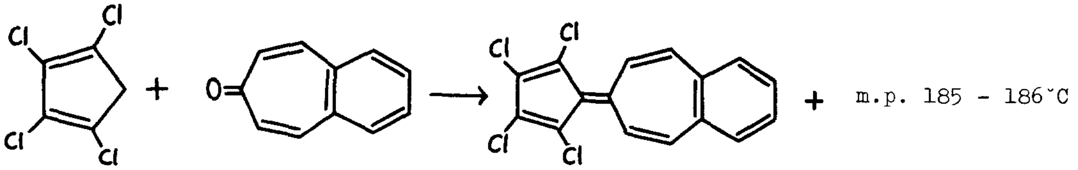
In the course of our study on sesquifulvalene chemistry, it has been reported that 1,2,3,4-tetrachlorobenzo[g]sesquifulvalene was obtained as a minor product by the reaction of benzo[d]tropone and 1,2,3,4-tetrachlorocyclopentadiene (1). We wish to communicate the unusual structure of the major product of this reaction.

A mixture of 3.12 g. of benzo[d]tropone (I), 4.08 g. of 1,2,3,4-tetrachlorocyclopentadiene (II) and 150 ml. of methanol was allowed to stand at 25°C. After



m.p. 185 - 186°C

(II) (I) (III) (IV)

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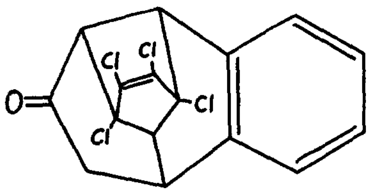
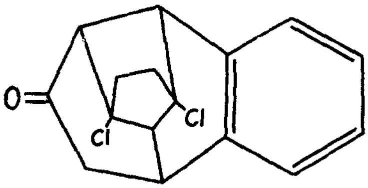
45 hr. the solution of this reaction mixture was turned to purple and the 0.15 g. of 1,2,3,4-tetrachlorobenzo[g]sesquifulvalene (III) were obtained as a purple needles. The major product (IV) was isolated by chromatography [alumina, ether] in a combined yield of 27.5%, as a colorless prisms, m.p. 185-186°C [from methanol]. Anal. Calcd. for $C_{16}H_{10}OCl_4$: C, 53.37; H, 2.79; mol. wt. 360. Found : C, 53.38; H, 2.84%; mol. wt. 378 [by Rast method]. The above data are clearly consistent with the apparent 1 : 1 adduct of I and II. The ultraviolet spectrum showed the bands typical to a benzene ring embedded in strained alicyclic framework at λ_{max}(cyclohexane) : 261 mμ (log ε, 2.51), 268 (2.63), 275.5 (2.64) (2). The infrared spectrum showed the bands of six-membered ring ketone at 1728 cm^{-1} and C=C double bond at 1619 cm^{-1}, and the n.m.r. spectrum [60 MHz, $CDCl_3$, TMS as an internal standard] exhibited a broad asymmetric four protons aromatic multiplet centered at δ 7.17 ppm, AB-quartet at δ 2.07 and 3.57 ppm (2H, J_{AB} = 15.5 Hz) and a complex multiplet at region of 3.0 - 3.8 ppm. (4H).

Catalytic hydrogenation of IV over Pd-C in methanol in the presence of sodium acetate provided, after uptake of three moles of hydrogen, a hydrogenated compounds (V) as a colorless prisms, m.p. 189-190°C, Anal. Calcd. for $C_{16}H_{14}OCl_2$; C, 65.54; H, 4.81. Found : C, 65.86; H, 4.90%, which retained the ultraviolet absorption at λ_{max}(cyclohexane) : 268 mμ (2.65), 275 (2.67) and the six-membered ring ketone at 1728 cm^{-1} in its infrared absorption spectrum but missing the band due to the C=C double bond. The n.m.r. spectrum exhibited an asymmetric multiplet centered at 7.13 ppm (4H, aromatic protons) and complex multiplet at a region of 1.5 - 3.9 ppm (10H). Taking account of the loss of two chlorine atoms and a double bond to the hydrogenation product suggests that IV



(A)



(B)

should have a tetrachlorocyclopentene structure; the two chlorines at bridge-head position and the remaining two at the double bond. On the basis of the above data, the cage structure (IV) and (V) were assigned to be (A) and (B) respectively.

Further conclusive evidence lies in a three dimensional X-ray diffraction study of V, which is crystallographically more convenient than the original product IV. Crystals of V are orthorhombic, with eight molecules an unit cell with the dimensions a = 23.95, b = 7.46 and c = 15.16 Å, the space group is Pbca. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs using $CuK\alpha$ radiation and measured visually against a standard scale. The independent reflections from 2592 planes were recorded. The crystal structure was determined by the symbolic addition procedure and refined by the least-squares method. After three cycles of refinement the R-factor was reduced to 0.14. The perspective drawing of the molecule is shown in Fig. 1. The original product IV should therefore be assigned structure shown above.

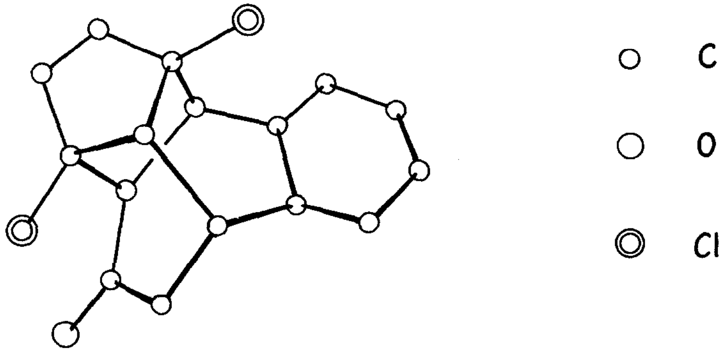


Fig. 1

The reaction might be initiated from the Michael type addition reaction of the tetrachlorocyclopentadienide ion to benzo[d]tropone and followed by an intramolecular Diels-Alder reaction to give a cage molecule (IV), as shown in Fig. 2.

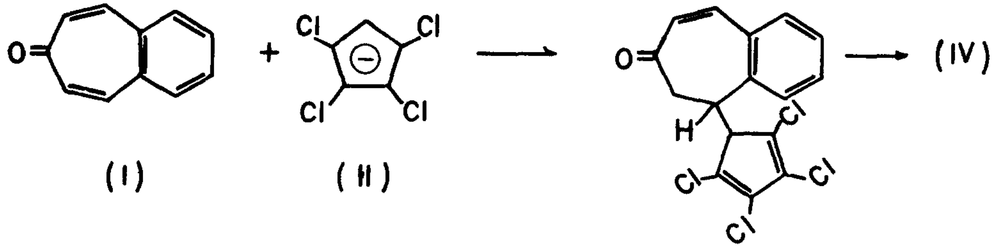


Fig. 2

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