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A CALICENE DERIVATIVE

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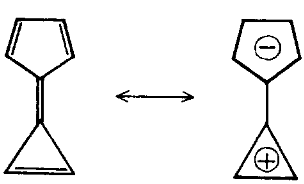
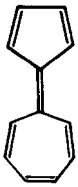
The cyclopropenylidene cyclopentadiene (calicene) (1) system (I) would be of interest from the theoretical and organic point of view because a significant contribution of ionic resonance form (Ia) to the ground state of I is similar to sesquifulvalene system (II).


(I) (Ia)

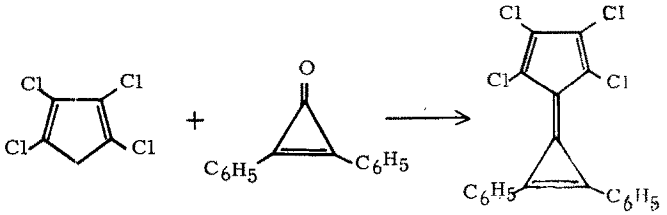

(II)

Using a simple HMO theory (2), it has been shown that I has large pi-electron delocalization energy and a stable closed-shell configuration. Recently several important contrrbutions (3, 4, 5) have been appeared and have prompted us to report herein our own independent study on the calicene system.

Our previous observation on the formation of substituted fulvenes (6) from 1, 2, 3, 4-tetrachlorocyclopentadiene (III) and tropone, and of 1, 2, 3, 4-tetrachloro-7, 8-benzosesquifulvalene (7) from III and 4, 5-benzotropone has told us to examine the use of stable diphenylcyclopropenone inplace of these tropones.

Reaction of III with diphenylcyclopropenone (IV) (8) at 30°C in methanol under nitrogen atmosphere afforded a crystalline product (V), yellow needles (from benzene), which shows no clear melting point, but gradually decomposes around 170°C, in 7. 5% yield.

Spectroscopic evidence described below as well as the analytical data (Found: C, 61. 31; H, 2. 69. Calcd. for $C_{20}H_{10}Cl_4$: C, 61. 22; H, 2. 55%) is consistent with the anticipated diphenyl-tetrachlorocalicene structure (V).



(III) (IV) (V)

In its infrared absorption spectrum there appeared a doublet at 1860 and 1828 cm^{-1} and a very intense absorption at 1525 cm^{-1} which is characteristic band of methylenecyclopropene (9).

The ultraviolet absorption spectrum of V showed a bathochromic shift of 9 mμ by the change of solvent from methanol to cyclohexane solution [λmax methanol: 338mμ (18, 000); λmax cyclohexane: 243 sh

(12, 500), 249 (13, 500), 254 (14, 500), 267 (16, 000), 347 mμ (33, 000)]. This solvent effect strongly support the contribution of ionic structure for the ground state of calicene system (3, 11).

Furthermore the absorption maximum of 347 mμ in cyclohexane is in good agreement with the calculated $A_1 \leftarrow A_1$ transition energy (3. 85 eV) of parent compound I obtained by the use of bond alternation model (10).

The nuclear magnetic resonance spectrum of V in deuteriochloroform (60 Mcps) showed single phenyl peak at 7. 21 ppm from internal tetramethylsilane, that in 95% sulfuric acid exhibited two multiplets centered at -1. 26 ppm and -0. 68 ppm from external benzene and singlet at +1. 42 ppm, the intensity ratio of these signals being 4 : 6 : 1. This suggests the structure protonated on the five-membered ring in acidic solution.

V is fairly basic and is extracted by 70% sulfuric acid from its benzene solution.

More detailed study and the X-ray analysis of this compound will be reported later.

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