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REACTION OF 1-ETHOXY-2,3-DI-<u>tert</u>-BUTYLCYCLOPROPENIUM FLUOROBORATE WITH SODIUM TETRACHLOROCYCLOPENTADIENIDE : FORMATION OF A DIHYDROPENTALENONE DERIVATIVE

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Reaction of 1-ethoxy-2,3-di-*tert*-butylcyclopropenium fluoroborate with sodium tetrachlorocyclopentadienide in methylene chloride gives 1,2-dihydro-2,3-di-*tert*-butyl-4,5,6-trichloropentalen-1-one along with 1,2,3,4-tetrachloro-5,6-di-*tert*-butylcalicene.

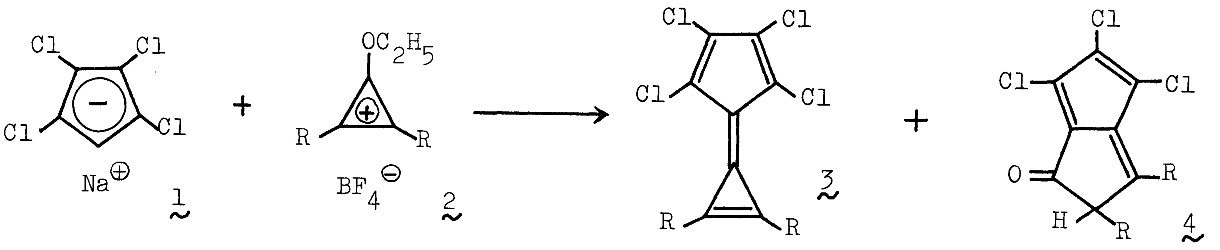
The reactions of the substituted cyclopropenones with tetrahalocyclopentadiene in methanol[1)] or the analogous reactions between the cyclopropenium and the cyclopentadienide ions[2)] have been extensively investigated with the intention of synthesizing the calicene (cyclopropenylidenecyclopentadiene) derivatives but none of the reactions leading to the formation of the rearranged product are known to date. We now report the first example of the formation of the dihydropentalenone derivative from the latter type of reaction.

To a solution of sodium tetrachlorocyclopentadienide (**1**) prepared from tetrachlorocyclopentadiene (8.07 mmol) and sodium hydride (10.50 mmol) in a mixed solvent of benzene (20 ml), methylene chloride (10 ml) and diglyme (3 ml) was added ethoxy-di-*tert*-butylcyclopropenium fluoroborate (**2**) (8.07 mmol) in methylene chloride (10 ml) at -35°C in an atmosphere of nitrogen for 30 min. Two products, **3**,[3)] colorless plates, mp 203-205°C (subl.), in 12.3% yield and **4**,[3)] orange needles, mp 172-174°C (d.), in 26.7% yield, were isolated after usual work-up followed by repeated column chromatography on alumina deactivated with 5% of water.

The minor product **3** was the expected calicene derivative as shown by the following spectral properties; uv. λ_{max} (EtOH) 220 nm (log ε 3.58), 317 (4.26), ir. ν_{max} (KBr) 1815, 1510 cm^{-1}, nmr (60 MHz, $CDCl_3$) δ 1.52 ppm (s, *tert*-butyl).
The structure of the major product was assigned as 1,2-dihydro-2,3-di-*tert*-butyl-4,5,6-trichloropentalen-1-one **4** on the basis of the spectral evidences. The ir spectrum of **4** shows strong carbonyl band at 1705 cm^{-1}. The uv spectrum of **4**, λ_{max} (EtOH) 235 nm (log ε 4.18), 265 (4.09), 332 (4.01) and 398 (3.46), implies the existence of fulvene chromophor.[4)] In its 60 MHz nmr spectrum ($CDCl_3$), two non-equivalent *tert*-butyl proton singlets and allylic methine proton singlet appear at δ 1.06 (9H), 1.50 (9H) and 3.35 (1H), respectively.

Conversion of **4** to pentalene derivatives has been examined but the expected enolization was not observed with various bases.[5)] When a solution of **4** in ethanol was treated with base such as potassium hydroxide or potassium *tert*-butoxide, a colorless solution was obtained which showed the ultraviolet absorption maxima at 215 and 315 nm. The dihydropentalenone 4 was regenerated unchanged from this solution upon treatment with hydrochloric acid. These behaviours may be accounted for by the reversible deprotonation and protonation between 4 and the cyclopentadienide 6. Predominant formation of 6 implies a thermodynamic instability of the pentalene structure 5.

In an attempt to obtain the immonium salt (7), a potential intermediate for the construction of the pentalene skeleton,[6] the dihydropentalenone derivative 4 was treated with dimethylamine in the presence of perchloric acid. The product isolated (70% yield) is, however, a dimethylamino-substituted derivative, $C_{18}H_{25}Cl_2NO$.[3] Structure 8 is tentatively assigned to this product based on the observed spectral properties : ir ν_{max} ($CHCl_3$)[7] 1660 cm^{-1}; uv λ_{max} (EtOH) 216 nm (log ε 4.42), 235 (4.31), 326 (4.15), 386 (3.67) and 457 (3.74); nmr (60 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.44 (s, 9H), 3.20 (s, 1H) and 3.27 (s, 6H). Compound 8 is also obtained through the reaction of 4 with dimethylamine in the absence of perchloric acid.



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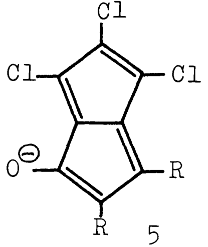

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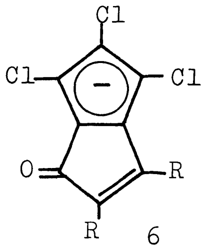

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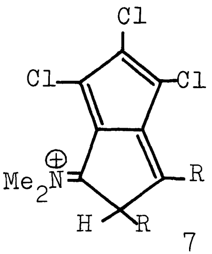

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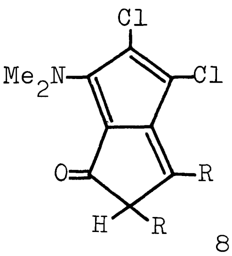

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2) A. S. Kende, P. T. Izzo, and P. MacGregor, J. Amer. Chem. Soc., 88, 3359 (1966).

3) All new compounds described in this paper gave satisfactory elemental analyses.

4) P. Yates in "Advances in Alicyclic Chemistry", Vol. 2, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N.Y., p. 59, 1968.

5) It has been shown that 3-(dimethylamino)-1(2H)-pentalenone can be converted with bases to the enolate.[6]

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7) It is well known that the presence of an amino group either substituted or unsubstituted on the β-carbon atom of an α,β-unsaturated ketone lowers the carbonyl band by 20-80 cm^{-1}. N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, J. Amer. Chem. Soc., 71, 3337 (1949).

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