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SYNTHESIS OF A BRIDGED HOMO[15]ANNULENIUM ION

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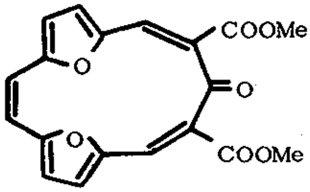
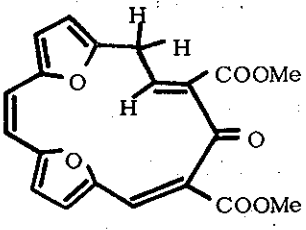
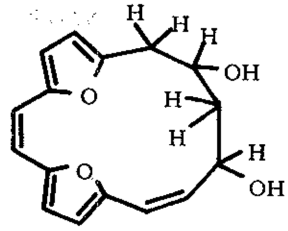
Ring expansion of 2,15-dimethoxycarbonyl[15]annulenone 4,7 : 10,13-dioxide **I** by dimethylsulfonium methylide gave rise to a 16-membered homo[15]annulene **II**, which was transformed to a diol **III** by a decarboxylation (copperchromite in quinoline)-reduction ($NaBH_4$) sequence. Compound **III** is considered to be a possible precursor of homo[15]annulenium ion, a 14π homoaromatic cation **IV**. As expected, **IV** in conc. H_2SO_4 at room temperature exhibited a characteristic spectrum, which is very similar to that of aromatic [15]annulenium tetrafluoroborate **V** [λ_{max} (in 30 % H_2SO_4) at 331 (110,000), 345 nm (10,800)], exhibiting absorption maxima (in conc. H_2SO_4) at 334 and 349 nm (33,000). This may be indicative of the occurrence of **IV**.


COOMe
O
O
O
COOMe

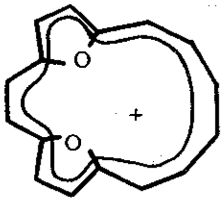
(I)


H
H
O
COOMe
H
O
O
O
COOMe

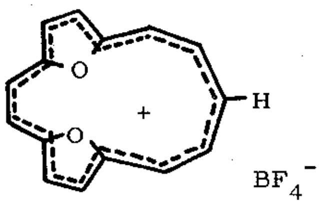
(II)


H
H
H
OH
O
H
H
O
H
OH

(III)


O
+
O

(IV)


O
+
H
O
BF_4^-

(V)