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CONSTRUCTION OF A [5]ANNULENO[15]ANNULENONE SYSTEM BY [14+2] CYCLOADDITION-DEHYDROGENATION SEQUENCE:** SYNTHESIS OF 15,16-DIMETHOXYCARBONYL-3,6:9,12-DIEPOXY-17-OXO-[12.2.1][5]ANNULENO-[15]ANNULENE†

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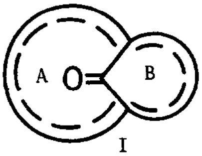
BICYCLIC annulenone I, in which the carbonyl group is shared by fused annulenone rings and is placed nearly planar with the plane of the resulting perimeter, is a novel class of annulene. I can be classified into four types according to the respective combinations of annulenones.



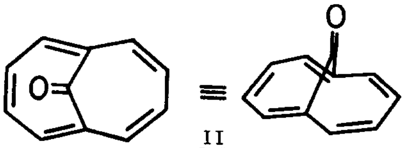
I

Annulenone A	Annulenone B	Extended Perimeter
$[4n+3]$	$[4n'+1]$	$[4N']$Annulene
$[4n+3]$	$[4n'+3]$	$[4N+2]$Annulene
$[4n+1]$	$[4n'+1]$	$[4N+2]$Annulene
$[4n+1]$	$[4n'+3]$	$[4N']$Annulene

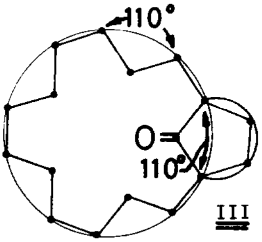
$N = n + n'$; $N' = N + 4$.

Studies on these groups of compounds of I are of considerable interest in the following respects; (1) electronic and magnetic effects of one annulenone to be exerted to the other and to the whole bicyclic system; (2) the ring current effects of I and its protonated species; and (3) the pK_a value and stability of the bicyclic hydroxyannulenium ion.

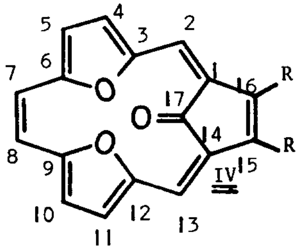
The only previously known compounds belonging to I is 1,6-methano[10]annulene-11-one II.[1,2] However, it was reported that the bridge carbonyl group and the 10π-electron system do not interact electronically to appreciable extent, since the carbonyl group is almost perpendicular to the perimeter. In contrast, scale drawing III, which is made up of fused regular pentagon and regular pentadecagon, suggests us that III is a planar and strain-free model to put the



II

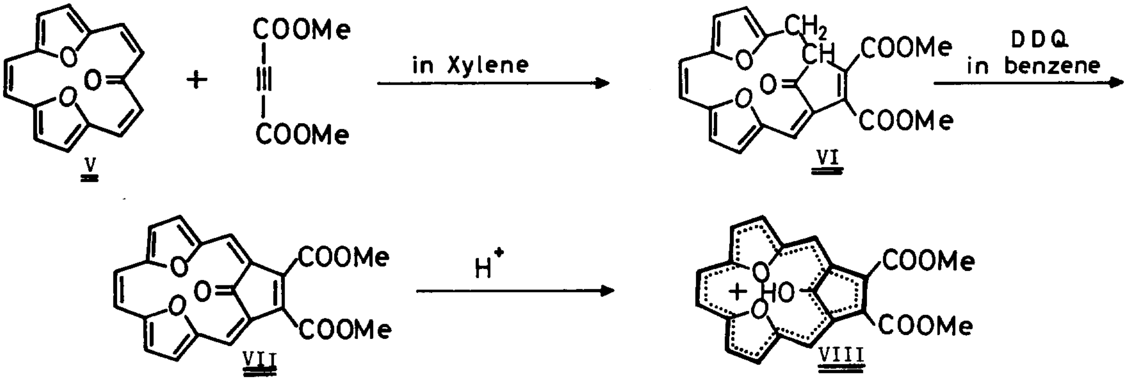


III



IV

carbonyl inwards on the molecular plane, since the outside angles of regular pentadecagon are exactly same with the inside angles of regular pentagon (110°). We now report the preparation and properties of a [5]annuleno[15]annulenone IV (R = COOMe), an oxygen-bridged model of III to be prepared. The synthesis could be reallized most simply by the following [14+2] cycloaddition-dehydrogenation sequence.



Heating of [15]annulenone dioxide V$^{3)}$ with 2.1 molar equivalent of dimethyl acetylenedicarboxylate in xylene for 10 hr, followed by chromatography on silica gel [benzene:ether = 3:1] gave in ca. 10.5% yield the di-ester VI as deep violet prisms, mp 164-5° (from MeOH), m/e 380 (M^+), λ_{max}^{MeOH} 241 nm (ε 14,100), 277 (18,900), 314 (28,100) and 526 (8,700); ir ν_{max}^{KBr} cm^{-1}: 1738 (ν c=o ester), 1700 and 1698 (ν c=o ketone). The di-ester was subsequently refluxed with DDQ (40 % excess) in benzene for 16 hr. Chromatography of the product on silica gel [CH_2Cl_2:ether = 100: 3] yielded 72.8 % of VII as bright black prisms, mp 196-8° (MeOH): m/e 378 (M^+);electronic spectrum, see Fig. 1; ir ν_{max}^{KBr} cm^{-1}: 1736 and 1727 (ν c=o ester), and 1700 (ν c=o ketone). Its nmr spectrum consists of very simple resonances due to C_{2v}-symmetry, confirming its structure (see Table I).

It is evident that VII is paratropic as compared with the nmr parameters of VI, all the outer proton resonances having moved to higher field (Δ = 0.58 - 1.17τ). Thus, new bicyclic system VII can be represented as a dioxido[16]annulene system. In agreement of this finding ir spectrum of VII provided also an interesting information. The position of the keto-carbonyl stretching band (1700 cm^{-1}) is very close to the corresponding value of cyclopentadienones$^{4)}$, but differs considerably from that of [15]annulenone dioxide V (1645 cm^{-1})$^{3)}$. This enable us to consider that the keto-carbonyl group of VII belongs preferentially to the cyclopentadienone ring rather than the [15]annulenone ring to facilitate the observed paratropicity of VII.

Obviously, it is also of interest to convert VII into the protonated species VIII and to

Table I. ^{1}H Nmr Parameters of the Fused Systems VI and VII in $CDCl_3$ (τ Values, Internal Standard TMS, J Values in Hz in Parentheses)

Compound	H-2, H-13	Furan (H-4,H-5, H-10, H-11)	H-7, H-8	COOMe	CH_2	CH
VI	3.13 s (H-13)	3.14 d (3.6) 3.37 d (3.6) 3.43 d (3.6) 3.59 d (3.6)	3.64 d (13.0) 3.86 d (13.0)	6.03 s 6.14 s	7.77 dd 1H (13.0, 9.0) 6.10-6.50 m, 1H	6.10- 6.50, m 1H
VII	4.28 s	4.01 d (3.6) 4.17 d (3.6)	4.81 s	6.24 s	——	——
Paramagnetic Shifts (Δ = VII - VI)	1.15	0.87 0.64 0.74 0.58	1.17 0.95	0.10	——	——

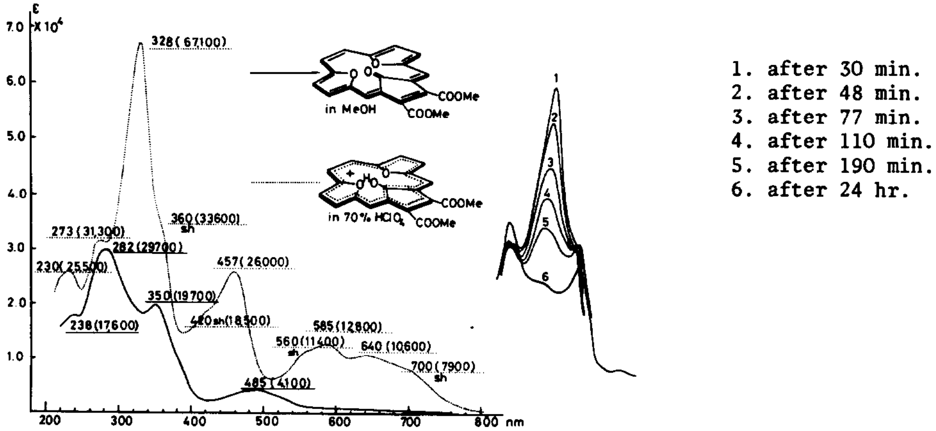


Figure 1. Electronic spectra of 15,16-dimethoxycarbonyl-3,6:9,12-diepoxy-17-oxo-[12.2.1][5]-annuleno[15]annulene VII and 15,16-dimethoxycarbonyl-3,6:9,12-diepoxy-17-hydroxy-[12.2.1][5]annuleno[15]annulenium ion VIII (after 15 min.). The spectral changes of VIII are showned on the right side of the spectra.

compare the criteria for aromaticity with those obtained from annulenoannulenes,$^{5,6)}$ since the expected ring current effect of the hydroxyannulenium ion VIII is stronger to a much greater extent than VII. Unfortunately, attempts to take a clean ^{1}H nmr spectrum of VIII has not been successful, because VIII decomposed rapidely in concentration so that the spectrum could be obtained (in CF_3COOD). However, electronic spectrum of VIII into 70 % $HClO_4$ gave an interesting information. An intensive absorption band reminiscent of that of the parent hydroxy[15]-annulenium ion (λ_{max} 337 nm (97,000) (in CF_3COOH)$^{7)}$ appears at 328 nm (calcd. ε value: 79,100, evaluated from first order kinetics from Fig. 1), together with a subsidiary peak at 457 nm. As showned in Fig.1, the electronic spectrum was transient, a progressive decrease of ε values having been observed in both 328 and 457 nm bands. Although, at present, we cannot imply the magnetic properties of VIII, the appearance of the prominent peak at 328 nm provides a strong indication that the chromophore of the 14π annulenium ion moiety is capable of exsistence as one of the contributor of VIII. We consider, the observed unstability of the hydroxy[15]-annulenium ion VIII (half life: $t_{1/2}$ = 62 min., at 28°C) is clearly responsible to an interaction to be occurred between the two ring systems, and, in part, to the precluded cis-trans equilibrium$^{8)}$ by the clamping ethylenic double bond.

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REFERENCES AND NOTES

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† Compound VII was named based on the nomenclature proposed by Prof. Sondheimer, see reference 6.

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