

CHEMICAL TRANSFORMATIONS OF 4:7,10:13-DIEPOXY[15]ANNULENONE
BY CARBONYL TRANSPOSITION REACTIONS

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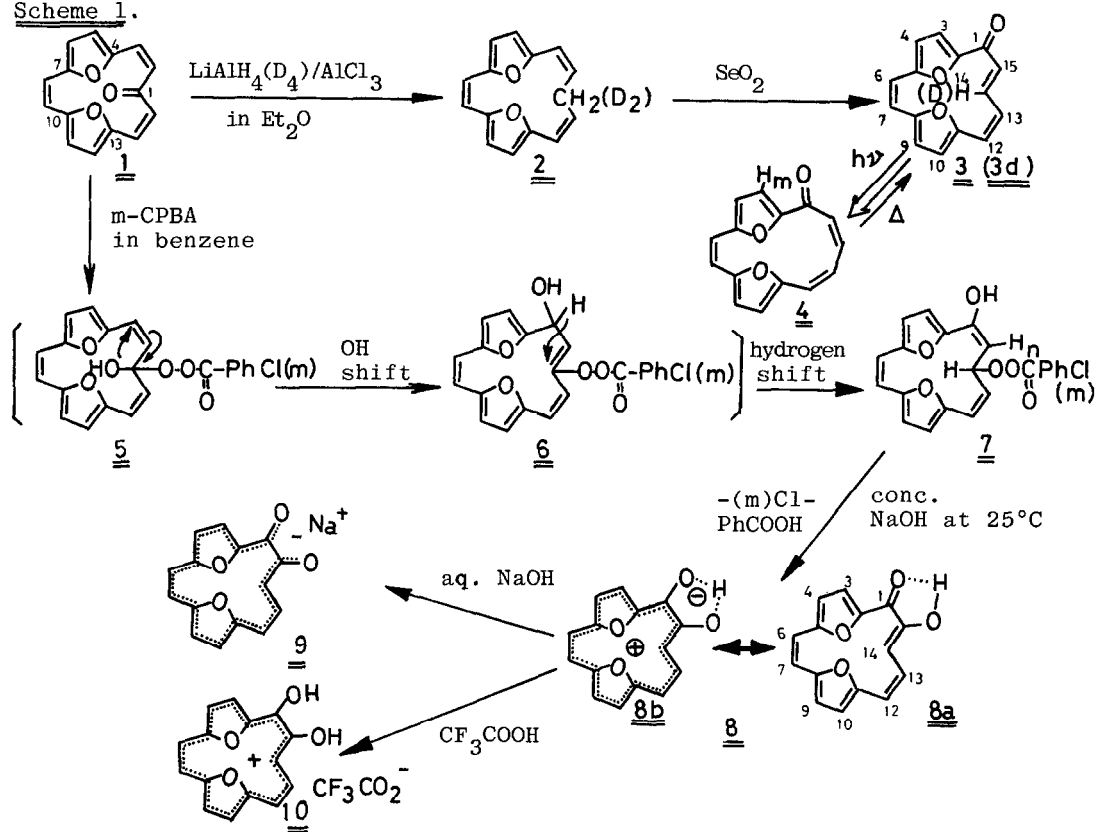
Abstract: The titled annulenone 1 could be converted into new annulenones 3 and 8 by carbonyl transposition reactions. Compound 8 can be regarded as the first 14π hydroxy-enone as a higher homolog of tropolone (6π) and hydroxy[11]annulenones (10π), and was proved to be aromatic.

Although annulenone 1¹⁾ is a simple molecule, it changes geometry through cis-trans isomerization as the consequences of the acceptance and/or the removal of environmental effectors such as light, heat and proton. This behaviour is quite similar to the coupled photo- and thermal isomerizations displayed by bacteriorhodopsin, in which retinal Schiff base acts as active center.²⁾ Being such isomerization susceptibility in annulenone 1 deeply correlative with structure, rates and equilibria of each isomerization step measured in modified annulenone frames (i.e. by skeletal rearrangements or alkyl and OH group introductions into the periphery) will give useful knowledge on the structure-isomerization relationships of the chemical cycle.

In the course of our investigations along this line, we have found that 1 could be transformed into carbonyl-position isomer 3 and its hydroxy derivative 8 by carbonyl transposition reactions. Synthetic values of these reactions are evident, since carbonyl-position-isomeric annulenones so far been prepared were synthesized according to independent synthetic principles, even if they are made up of same building blocks.³⁾

On reduction with $\text{LiAlH}_4/\text{AlCl}_3$ (at $-10^\circ\text{C} \sim -5^\circ\text{C}$, 5 min) 1 gave unstable dioxo-compound 2⁴⁾ (m.p. 110°C), which is purified by chromatography (SiO_2 , CH_2Cl_2) and immediately oxidized with SeO_2 in pyridine to give 3 [m.p. 184°C , 23%

Scheme 1.



yield (based on **1**); Mass 238 (M^+); IR (KBr) 1620 cm^{-1} ($\nu\text{C}=\text{O}$); UV λ_{max} (CH_2Cl_2) 303 nm (ϵ 26,800), 406 (6,500), and 428 (6,100)]. The comparison of the ^1H -NMR data collected from **3** and the corresponding deuterated species **3d**, which was prepared by LiAlD_4 in stead of LiAlH_4 , confirmed the structure. Undeuterated species **3** exhibited the H-14 proton as a multiplet at δ 6.10 and the H-15 proton as a doublet at δ 7.02 ($J = 16.7\text{ Hz}$), whereas the deuterated species **3d** did not show the H-14 proton signal, but shows the H-15 proton as a singlet at δ 7.00. Furan proton H-3 is deshielded by ca. 0.6 ppm ($\delta = 7.90\text{ d}$), as compared with other furan protons at H-4,9 and 10, indicating that the H-3 proton in **3** resides in a deshielding region of the new annulenone ring as the consequence of the mono-*trans* conformation (Table I).

On irradiation (750 W projector lamp, at 0°C , 1 hr in $\text{CCl}_4/\text{Et}_2\text{O} = 1:1$) **3** was isomerized into the all *cis* congener **4** (purified by chromatography on a basic alumina column, $\text{CCl}_4/\text{Et}_2\text{O} = 1:1$), which was stable only in solution. On evaporation the solvent, rapid isomerisation took place to regenerate **3**. The ^1H -NMR spectrum of **4** indicated that all of the proton signals moves to ca. 0.8

ppm higher field, appearing 9H protons at 6.10~6.40 ppm, and 1H furan proton (H_m , see Scheme 1) at 7.13 ppm (d, $J = 3.7$ Hz) suggesting that 4 sustains no ring current, and that 4 occupies a puckered conformation.

The keto-hydroxy compound 8 could be prepared as follows: 1 was allowed to react with m-chloroperbenzoic acid (2.5 molar excess) for 24 hr in benzene at 25°C. After washing of the reaction mixture with aq. Na_2SO_3 solution, chromatographic separation gave an unseparable enantiomeric mixture of 7 [m.p. 95 - 98°C, 26% yield; Mass 410 (M^+); IR (KBr) 1725 ($\nu_{C=O}$) and 3450 cm^{-1} (ν_{OH})]. The 1H -NMR spectrum of 7 (in $CDCl_3$) exhibited two separated complex signal groups appearing at δ 5.85 - 6.80 [proton integration 8H (4H furan protons + 4H olefinic protons)] and at 7.20 - 8.20 [proton integration 4H, benzenoid protons]. Three poorly resolved but characteristic proton signals appearing at δ 3.65, 4.14 and 4.90 were assigned as the OH (1H, br. m.), the methine proton (1H, m.) and H_n proton (see Scheme 1, 1H. m.), respectively. For the formation of 7, the rearrangement mechanism shown in Scheme 1 was postulated. As was anticipated, on treatment of 7 with aq. conc. NaOH at 25°C a rapid removal of m-chlorobenzoic acid took place to give 8 in 27% yield [m.p. 195°C; Mass 254 (M^+), λ_{max} (CH_2Cl_2) 233 (19,000), 324 (54,700), 352 (27,000), 375 (8,160), 422 (9,140), 443 (10,300), 472 (9,140), and 508 nm (6,670)]. That 8 is common in geometry with 3, but one OH group is introduced to partake an intramolecular H-bonding with the C=O group was confirmed by following findings. Like 3, the H-3 proton was deshielded ca. 0.8 - 1.2 ppm as compared with other furan protons (H-4, 9 and 10) (Table I). Diatropicity of 8 becomes greater than that of 3, since chemical shift difference of [$\Delta\delta = \delta(H-3) - \delta(H-14)$] is greater in 8 ($\Delta\delta = 4.91$ ppm) than in 3 ($\Delta\delta = 1.80$ ppm) (see Table I). The IR spectrum of 8 is typical of an aromatic hydroxy-

Table I. The 1H -NMR Spectral Data of Compounds 3 and 8

Proton	in <u>3</u> in CD_2Cl_2	in <u>8</u> in $CDCl_3$
H-3 (furan proton)	7.90, d. ($J = 3.9$ Hz)	8.39, d. ($J = 3.9$ Hz)
H-4, 9 and 10 (furan protons)	7.23, d. ($J = 3.9$ Hz)	7.27, d. ($J = 3.9$ Hz)
	7.29, d. ($J = 3.9$ Hz)	7.56, d. ($J = 3.9$ Hz)
	7.31, d. ($J = 3.9$ Hz)	7.61, d. ($J = 3.9$ Hz)
H-6 and 7	7.04, s.	7.43, s.
H-12	7.27, m.	7.54, d. ($J = 10.1$ Hz)
H-13	7.27, m.	8.00, q. ($J = 12.8$ Hz, 10.1 Hz)
H-14	6.10, m.	3.48, d. ($J = 12.8$ Hz)
H-15	7.02, d. ($J = 16.7$ Hz)	—
OH	—	7.90, a broad singlet

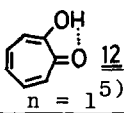
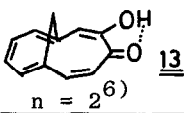
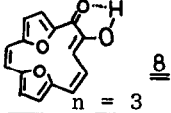
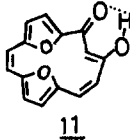
enone (Table II). The observed carbonyl frequency was shifted ca. 60 cm^{-1} to a lower value than that of 3, indicating that the H-bonding increases participation of dipolar form 8b. The OH group in 8 is more acidic ($\text{pK}_a = 9.0$, by spectroscopic titrations in $\text{EtOH} : \text{H}_2\text{O} = 1:1$) than that of phenol ($\text{pK}_a = 10.0$).

On addition of aq. NaOH 8 forms a reddish brown anion 9 (λ_{max} 340 (48,500), 373 (28,300), 454 (11,250), 469 (14,600), and 558 nm (4,300)). The carbonyl group is protonated in CF_3COOH to form 14 π annulenylion 10 [λ_{max} 253 (18,000), 350 (133,600), 449 (10,500), 500 (22,180), and 531 nm (5,760)]. The appearance of a dark colour with FeCl_3 solution indicates that 8 forms a Fe-complex.

Thus, properties of 8 are, in all respects, in harmony with those of the smaller hydroxy[4n+3]annulenone homologs, tropolone 12 ($n = 1$)⁵ and two isomeric hydroxy[11]annulenones ($n = 2$, e. g., 13)⁶. 8 is a new Hückel aromatic, whose properties are to be dominated by Hückel rule as the first example of $n = 3$ member.

Finally we may expect a continuation of interest in the synthesis of a variety of isomeric annulenones composed of both [4n+1]- and [4n+3]annulenones by carbonyl transposition reactions. The synthesis of isomeric hydroxy-annulenone, such as 11, has to be expected, since rates and isomerization equilibria of 11 is expected to be very different from those of 1 and 8 throughout each step of the conformational changes.

Table II. Properties of Hydroxy[4n+3]annulenones ($n = 1, 2$ and 3).

[4n+3]-annulenone	 <u>12</u> $n = 1$ ⁵	 <u>13</u> $n = 2$ ⁶	 <u>8</u> $n = 3$	 <u>11</u>
IR (cm^{-1})	1618 ($\nu\text{C=O}$) 1550 ($\nu\text{C=O}$) (CCl_4)	1518, 1536 ($\nu\text{C=O}$) 1558, 1577 and $\nu\text{C=C}$ 3290 (νOH) (KBr)	1560 ($\nu\text{C=O}$) 3285 (νOH) (KBr)	
pK_a (in H_2O) pK_a (in $\text{EtOH} : \text{H}_2\text{O}$ $= 1:1$)	6.7* 8.2*	8.25	9.0*	
		* from present measurements		

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(Received in Japan 27 August 1985)