CYCLOADDITIONS OF 1,5- AND 1,7-AZULENEQUINONES TO BENZO[*c*]FURAN AND ITS 1,3-DIPHENYL DERIVATIVE

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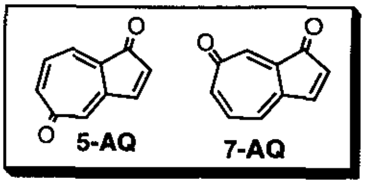
Abstract—With 1,3-diphenylbenzo[*c*]furan (DIBF), 1,5-azulenequinone (5-AQ) gave a [2+4] cycloadduct and a [2+4]-[6+4] cycloadduct which were interconverted under mild conditions. This is the first observation of conjugated rearrangement of [2+4] mode to [6+4] mode with the second attack of cycloaddend or conjugated cycloreversion with the rearrangement. 1,7-Azulenequinone (7-AQ) formed two stereoisomeric 1:2-[2+4]-[6+4] cycloadducts. With benzo[*c*]furan, 5-AQ and 7-AQ afforded two and four stereoisomeric [2+4]-[6+4] cycloadducts, respectively.

In 1984, Scott *et al.*[1] reported the cycloadditions of 1,5- and 1,7-azulenequinones (5-AQ and 7-AQ) to 1,3-diphenylbenzo[*c*]furan (DIBF) to afford the sole 1:2-[2+4]-[6+4][2] cycloadducts.

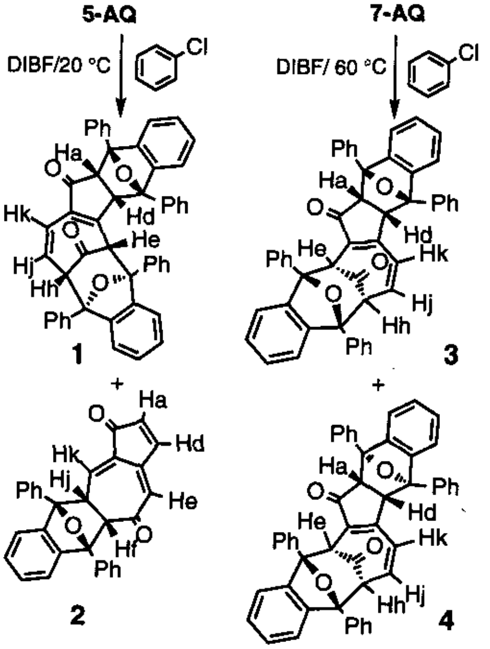
Recently, we have investigated the high-pressure-acceleration of Diels-Alder reactions of 3-bromo-1,5-azulenequinone and 3-bromo-1,7-azulenequinone (BAQ, B-5-AQ and B-7-AQ) with several dienophiles to observe the exclusive [4+2] cycloaddition process.[3]

We have also investigated the thermal cycloaddition reactions of BAQ with benzo[*c*]furan (IBF)[4] and DIBF;[5] the results were quite different from one to another.



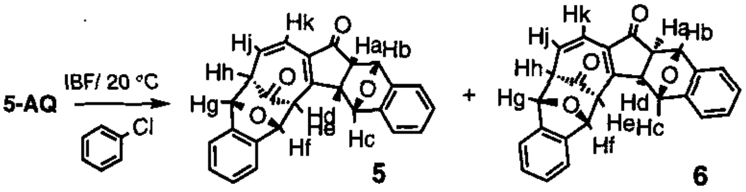
These all prompted us to extend the study to the parent AQ, which were obtained by catalytic hydrogenation of BAQ (with Pd / C), and DIBF and/or IBF, and the results are described herein.

The cycloaddition of 5-AQ with DIBF yielded a 1:2-product (**1**, colorless crystals, mp 117-118 °C (lit.,[1] 139-140 °C), 40% yield), and a 1:1-product (**2**, a colorless oil, 5% yield); the identity of **1** with the Scott's product was confirmed by ^{1}H nmr spectral comparisons,[1] and its stereochemistry was deduced to be the *anti-exo*-[6+4]-*endo*-[2+4] structure by comparisons with a series of cycloadducts obtained from BAQ.[4]

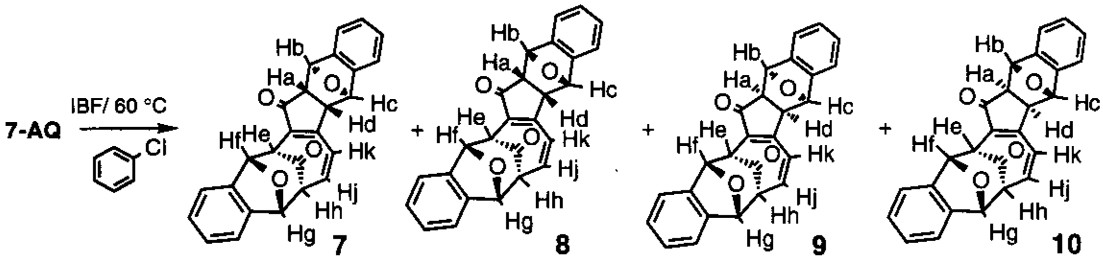


The ^{1}H nmr spectrum indicated that **2** is a [2+4] cycloadduct at the tropone moiety; two vicinal methine protons at δ=4.15 and 4.83 (J=8.4 Hz). The cyclopentenone moiety is intact since the signals at δ=6.86 and 7.06 (J=5.1 Hz) remained almost unchanged.

The reaction of 7-AQ with DIBF gave 1:2-cycloadducts (**3**, colorless crystals, mp 173-175 °C, 46% yield, and **4**, colorless crystals, mp 228-229 °C (lit.,[1] 122-124 °C), 17% yield), whose stereochemistries were established from the nmr chemical shift comparisons with the corresponding Br derivatives. Under our conditions, **3** was the major product, and the other, **4**, might be the Scott's product.[1] Comparisons of their ^{13}C nmr spectra with those of two cycloadducts obtained from B-7-AQ confirmed that they belong to the same stereostructural categories. Unlike **1**, both **3** and **4** were inert against the cycloreversion.



Similar treatment of IBF with 5-AQ afforded two stereoisomeric [2+4]-[6+4] cycloadducts (**5**, colorless crystals, mp 165-168 °C, 48%, and **6**, colorless crystals, mp 276-278 °C, 29% yield), and with 7-AQ did four [2+4]-[6+4] cycloadducts (**7**, colorless crystals, mp 245-247 °C, 45%, and **8**, colorless crystals, mp 242-244 °C, 13%, **9**, colorless crystals, mp 191-194 °C, 21%, and **10**, colorless crystals, mp 180-182 °C, 9%), respectively. One notable feature is that the **Hf** of **9** at δ=4.07 appeared at considerably higher field than those of **7**, **8**, and **10**. This high-field shifted signal for **Hf** (δ= 4.10) was noticed in the *syn-endo*-[4+2]-*exo*-[6+4] cycloadduct from B-7-AQ.[4] The structures of other compounds were also established by detailed nmr spectral analyses, including the chemical shift comparisons with the corresponding Br derivatives.



Some of the figures show considerable differences, but they could be explained in terms of the substitution effect of Br in the BAQ series. All the ^{1}H nmr spectral data of cycloadducts were compiled in Table 1.

Table 1. The ^{1}H nmr chemical shift data with selected J -values of **1—10** (in $CDCl_3$, 270 MHz)[a]

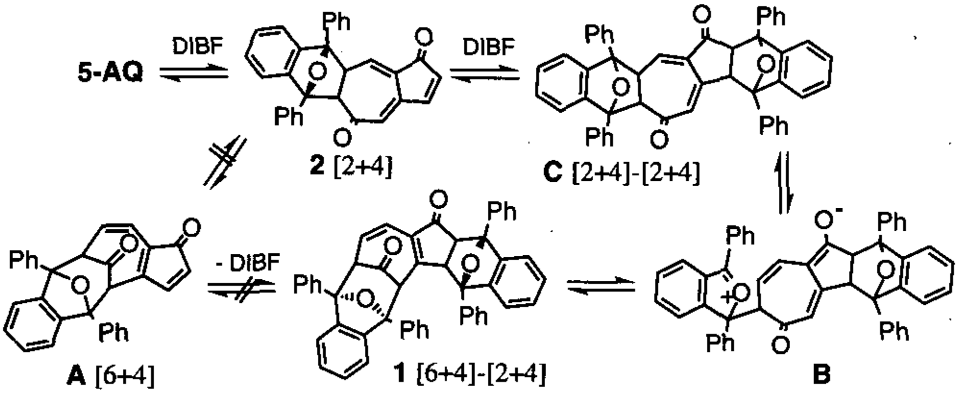
	Ha	Hb	Hc	Hd	He	Hf	Hg	Hh	Hj	Hk	
1	3.45	Ph	Ph	3.07	4.12	Ph	Ph	3.83	5.42	5.86	(J_{ad}=6.2; J_{fg}=1.8; J_{hj}=7.3)
2	6.86	-	-	7.06	7.09	4.15	Ph	Ph	4.83	7.09	(J_{ad}=5.1; J_{fj}=8.4)
3	3.58	Ph	Ph	4.52	3.83	Ph	Ph	3.88	5.76	6.08	(J_{ad}=6.6; J_{eh}=2.2; J_{hj}=7.0)
	(+0.35)	-	-	(Br)	(-0.05)	-	-	(+0.17)	(+0.32)	(+0.50)	
4	3.02	Ph	Ph	3.39	4.35	Ph	Ph	3.78	5.25	5.60	(J_{ad}=5.5; J_{eh}=1.8; J_{hj}=7.7)
	(+0.24)	-	-	(Br)	(+0.08)	-	-	(+0.09)	(+0.04)	(-0.04)	
5	3.61	5.61	5.67	4.00	3.38	5.59	5.35	3.20	5.75	5.97	(J_{ab}=J_{ad}=6.2; J_{ef}=1.5; J_{gh}=1.8)
	(+0.32)	(+0.09)	(0.00)	(Br)	(+0.15)	(+0.73)	(-0.02)	(+0.07)	(+0.11)	(+0.02)	
6	2.78	5.50	5.29	3.14	3.70	5.58	5.50	3.46	6.06	6.56	(J_{ab}=0; J_{ad}=5.1; J_{ef}=J_{gh}=1.8; J_{fg}=0)
	(+0.10)	(+0.06)	(+0.22)	(Br)	(+0.45)	(+0.21)	(-0.03)	(+0.05)	+0.12)	(+0.02)	
7	3.01	5.54	5.33	2.69	3.76	5.48	5.40	3.51	6.47	6.55	(J_{ab}=1.1; J_{ad}=5.5; J_{ef}=J_{gh}=1.5; J_{fg}=0)
8	3.58	5.58	5.52	3.96	2.98	5.34	5.18	3.25	6.30	6.32	(J_{ab}=J_{ad}=6.2; J_{ef}=2.2; J_{fg}=0; J_{gh}=1.5)
	(+0.35)	(+0.12)	(+0.05)	(Br)	(+0.05)	(+0.04)	(+0.03)	(+0.03)	(+0.15)	(+0.22)	
9	3.55	5.61	5.38	3.84	3.26	4.07	5.20	3.33	6.28	6.28	(J_{ab}=J_{ad}=6.2; J_{ef}=J_{gh}=1.5; J_{fg}=0)
	(+0.36)	(+0.12)	(+0.25)	(Br)	(+0.03)	(+0.03)	(+0.03)	(+0.09)	(+0.14)	(+0.23)	
10	2.72	5.13	5.44	3.10	3.80	5.48	5.41	3.51	6.48	6.54	(J_{ab}=0; J_{ad}=5.5; J_{cf}=J_{gh}=1.5)

[a] The chemical shift differences, Δδ, are shown in parentheses, and the positive values indicate high-field shifts for those of cycloadducts from AQ.

Thus, AQ behaved quite differently from BAQ to give the products with different mode.

Surprisingly, **1** and **2** were interconvertible; even during the silica gel column chromatography or standing in benzene solution, **1** gave **2** and DIBF, and standing a mixture of **2** and DIBF in $CDCl_3$ at 60 °C gradually afforded **1**. No other compound could be detected during the reaction. In this interconversion, a change of the mode, [6+4] to [2+4], occurred *via* a fomal 1,5-sigmatropic rearrangement.

The direct cycloreversion of **1** to **2** requires a generation of highly reactive cyclopentadienone intermediate (**A**),[6] and this should be disfavorable. On the other hand, the *syn-exo*-[6+4]-*endo*-[2+4] stereochemistry for **1** possesses severe steric hindrance between phenyl groups on the bridge-head, which may facilitate the rearrangement *via* intermediates such as **B** and **C**; the positive charge on the oxygen is delocalizable to two phenyl groups on the conjugated positions. This, although being tentative, is consistent with the phenomenon observed only with 5-AQ and DIBF (Scheme 1).[7] Detailed discussions should be a matter of full paper. In monocyclic tropone derivatives, thermal [6+4]-to-[4+2] rearrangement was frequently observed,[8] but the [6+4]-to-[2+4] or [2+4]-to-[6+4] rearrangement has not been recorded.



Scheme 1. Interconversion of **1** and **2**.

One of the authors (T. N.) wishes to thank Prof. Klaus Hafner, Technische Hochschüle Darmstadt, for his generous donation of the starting material, azulene.

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2. The term, [m+n], denotes the mode of the reaction between mπ of AQ and nπ of the counterpart.
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6. The AQ hitherto isolated are only derivatives having no cyclopentadienone moiety. See *e.g.*, M. Morita and K. Takase, *Chem. Lett.*, **1978**, 513; Y. Matsubara, H. Yamamoto, and T. Nozoe, "Studies on Natural Product Chemistry", Vol. 14, ed. by Atta-ur-Rahman, Elsevier, Amsterdam, 1994, pp.313-354.
7. One shoud notice that stereospecific formation of **1** from DIBF and 5-AQ is attributable to the conjugated nature of [1,5] sigmatropy and second [2+4] cycloaddition step; others, all 1:2-cycloadduct formations are non-stereospecific.
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Received, 13th November, 1995