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Products of the addition of 1,4-naphthoquinone to an acecyclone

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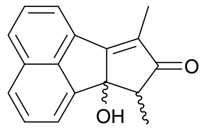
Abstract—The major products from the exposure of tetracyclic keto-alcohol **1** to excess 1,4-naphthoquinone in the presence of acid were a hexacyclic quinone (**6**) and a heptacyclic dihydrobenzofuran derivative (**8**).

In 1952, Allan and VanAllen[1] prepared tetracyclic keto-alcohol **1** by the condensation of acenaphthenequinone with 3-pentanone. The addition of acid to **1** produced acecyclone **2**, which dimerized by *endo* addition to compound **3**.[1–3] Heating **3** led to the *exo* adduct by equilibration (via reversion to **2**)[2] and to **4** by the loss of carbon monoxide.[3,4]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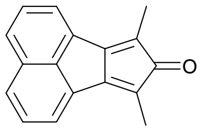
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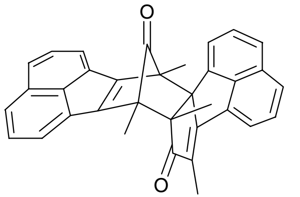
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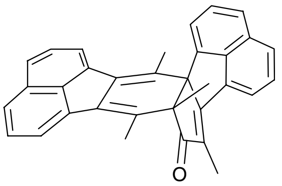
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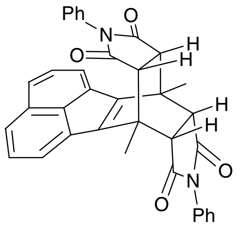
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Acecyclone **2** has been intercepted many times by dienophiles,[1–5] and the products were often not the simple Diels–Alder adducts, but the double adducts. For instance, heating **3** with *N*-phenylmaleimide yielded **5**.[2] Facile loss of carbon monoxide from the initial adduct led to a cyclohexadiene that added a second molecule of the dienophile. The stereochemistry of **5** indicated that both Diels–Alder reactions proceeded through *endo* transition state geometries.

A benzene solution of keto-alcohol **1** with 2.1 molar equivalents of 1,4-naphthoquinone and a catalytic amount of *p*-toluenesulfonic acid was heated under reflux for 22 h. Flash column chromatography and crystallization were used to purify the two major products, but neither was the expected double-addition product.

The less polar product was obtained as bright yellow needles in a 27% yield.[6] The ^{1}H NMR spectrum of this material was comprised of a set of signals attributable to an acenaphthalene moiety, two signals due to the 1,4-naphthoquinone unit and one singlet that arose from two methyl groups. Integration of the spectrum showed that the proportions of **2** and the 1,4-naphthoquinone were 1:1. The mass spectrum of the compound showed a strong molecular ion at m/z 360. These data led to the assignment of **6** as the structure. It appears that following a Diels–Alder addition with the quinone to provide **7**, carbon monoxide was expelled to give the expected diene, but then, instead of a second Diels–Alder reaction taking place with another molecule of 1,4-naphthoquinone, the diene aromatized to the hydroquinone, and a second molecule of 1,4-naphthoquinone oxidized this to quinone **6**. Sygula and co-workers[7]

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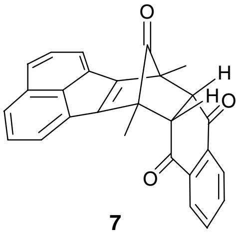
cleverly exploited a similar reaction in the synthesis of a dicorannulenobarrelene.



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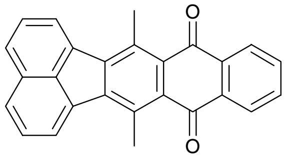
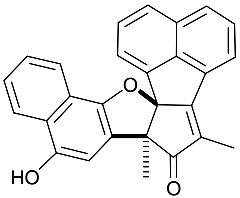


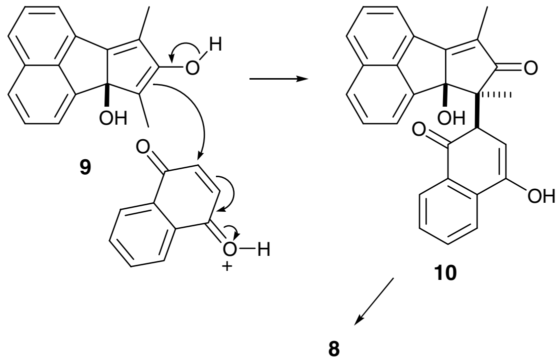
6

The more polar product (51% yield) was obtained as orange-red crystals.[6] The NMR spectra indicated an unsymmetrical 1:1 adduct, but overlap precluded a detailed analysis. The mass spectrum showed a strong molecular ion at *m*/*z* 390, a mass that indicated that the molecule had not liberated carbon monoxide and was reluctant to do so. X-ray crystallography[8] provided structure **8** (Fig. 1).



8

The structures of **2** and 1,4-naphthoquinone preclude a precedented partway to this dihydrobenzofuran. Dihydrobenzofurans can be produced when a β-hetero-substituted enone, typically a β-aminoenone, reacts with a quinone.[9] The electron-rich alkene attacks the quinone in a 1,4-manner, and then the quinone oxygen closes onto the intermediate stabilized cation (an iminium ion in the case of a β-aminoenone). A second pathway requires a 2-acetyl quinone, which reacts in a 4+2 manner as a heterodiene with the enol form of a β-dicarbonyl, and the dihydropyran adduct rearranges readily to the dihydrobenzofuran.[10] A third process begins with a Diels–Alder reaction between the quinone and a 1-oxygen-substituted diene. Under acid catalysis, cleavage of the newly formed carbon–carbon bond of the adduct proximal to the oxygen substituent of the diene takes place as the oxygen substituent becomes the carbonyl of an enone. An oxygen of the quinone moiety adds to the β-position of the enone to close the five-membered ring.[11] Given the reactivity of **2**, it might be tempting to assume that **8** was derived from the Diels–Alder adduct **7**, that is, the third pathway to the dihydrobenzofuran was followed. However, apart from the lack of an appropriately placed oxygen in the adduct, elimination of carbon monoxide from the adducts of **2** has been observed to be facile, and so cleavage of one of the new σ-bonds on **7** would be unlikely. It can only be conjectured that either the antiaromatic nature of the cyclopentadienone moiety of **2** encourages an initial 1,4-attack on **2** by the quinone's oxygen, or, more likely, that **2** is not an intermediate in the formation of **8** (Scheme 1). The addition to naphthoquinone, in a 1,4-manner, by the convex face of **9**, the enol form of **1**, would give intermediate **10**. The hydroxyl group of **10**, even though it is tertiary, would be well positioned to form a hemiacetal with the ketone, and elimination of water would provide **8**, with a cis-geometry across the new ring junction.



Scheme 1. Suggested pathway leading to **8**.

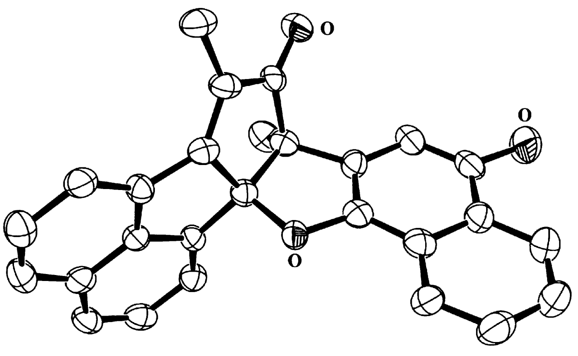


Figure 1. X-ray crystal structure of **8**.

Acknowledgement

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6. For compound **6**: mp 290–292 °C; IR (cast) 1657 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.35 (2H, d, $J = 7.2$ Hz), 8.16 (2H, dd, $J = 5.7$, 3.4 Hz), 7.96 (2H, d, $J = 8.1$ Hz), 7.74 (2H, dd, $J = 5.7$, 3.4 Hz), 7.73 (2H, dd, $J = 8.1$, 7.2 Hz), 3.22 (6H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 184.3 (very weak), 143.6, 136.2, 136.0, 134.9, 134.6 (very weak), 133.6,

133.2, 129.8, 128.2, 126.2, 126.0, 19.0. For compound **8**: mp 206–208 °C; IR (cast) 3372, 1705, 1662, 1595 cm^{-1}; ^{1}H NMR (CD_3SOCD_3, 300 MHz) δ 10.1 (1H, s), 8.14–7.26 (m), 6.95 (1H, s), 2.04 (3H, s), 1.57 (3H, s); ^{13}C NMR (CD_3SOCD_3, 75 MHz) δ 206.5, 167.3, 148.5, 145.2, 139.7, 136.5, 134.1, 133.0, 131.3, 129.2, 128.6, 128.5, 126.9, 126.5, 125.4, 123.1, 122.3, 121.6, 121.0, 120.4, 103.3, 58.8, 18.9, 9.3.

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8. Crystallographic data (excluding structure factors) for compound **8** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 298099. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.
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