

Procedures and Data

Reaction of Cyclooctyne with Fischer Carbene Complexes – Synthesis of Tricyclic Quinone Derivatives

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Abstract. Thermal reaction of Fischer carbene complexes **1**–**3** with cyclooctyne **4** followed by oxidation with Ce(IV)am-

monium nitrate furnished tricyclic quinone derivatives **5**–**7** incorporating an eight-membered ring.

The Dötz benzannulation reaction of Fischer carbene complexes with alkynes leads in a highly flexible manner to hydroquinone chromium complexes or after oxidation to quinone derivatives [1]. This new process for the construction of oxygenated six-membered compounds has frequently been applied to complex syntheses [2]. Surprisingly, no cyclic alkynes have been studied so far in this reaction. Due to our interest in benzannulated cyclooctane derivatives [3] we briefly examined the suitability of cyclooctyne **4** as substrate in the Dötz reaction, which is the lowest isolable member of the cycloalkynes [4].

be anticipated that larger cycloalkynes behave similar. On the other hand, it might be highly interesting to study *in situ* generated more strained cycloalkynes such as cycloheptyne, cyclohexyne or even arynes [5].

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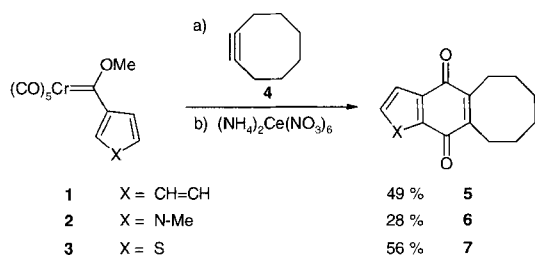
Experimental

Starting materials: **1** [6], **2** [7], **3** [8], **4** [9]. For general information see [10].

General Procedure: Under an atmosphere of argon a solution of the carbene complex and cyclooctyne in 10 ml of THF was heated at 66 °C for 5 h. After evaporation of the solvent the crude product was dissolved in 40 ml of CH₂Cl₂ and stirred with a solution of (NH₄)₂Ce(NO₃)₆ in 80 ml of water. After 30 min the organic layer was separated and extracted with water (80 ml) and brine (40 ml). The organic phase was dried (MgSO₄) and filtered through a pad of celite (elution with hexane/EtOAc = 10:1) furnishing after evaporation the crude product (yellow-brownish crystals) which was purified by chromatography (hexane/EtOAc = 15:1) on alumina.

6,7,8,9,10-Hexahydro-cyclo[b]naphthalene-5,12-dione (**5**)

According to the general procedure, 624 mg (2.00 mmol) of **1** and 325 mg (3.00 mmol) of **4** gave a crude product which was



Carbene complexes **1**–**3** which are easily available by the classical Fischer route were heated with 1.5 equivalents of **4** in dry tetrahydrofuran. After exchange of the solvent the crude mixture was oxidized with Ce(IV)ammonium nitrate. Chromatographic purification afforded the desired new tricyclic quinone derivatives **5**–**7** as yellow or orange crystals in high purity. The moderate to good overall yields achieved demonstrate that no particular effects are complicating the Dötz reaction of the considerably strained cyclooctyne, and it can

oxidized with 11.0 g (20.0 mmol) of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Chromatography furnished 233 mg (49%) of **5** as yellow crystals (*m.p.* 92–94 °C). – $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ/ppm = 8.06, 7.68 (2 m, 2H each, =CH), 2.79 (m, 4H, 2CH₂), 1.90–1.64, 1.60–1.42 (2 m, 4H each, 4CH₂). – $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ/ppm = 184.3 (s, C=O), 147.3, 132.3 (2 s, quinone-C), 133.1, 126.1 (2 d, =CH), 29.8, 26.6, 25.2 (3 t, CH₂). – IR (KBr): ν/cm^{-1} = 2925, 2820 (=C–H, C–H), 1655 (C=O), 1615, 1595 (C=C).

$\text{C}_{16}\text{H}_{16}\text{O}_2$ Calcd.: C 79.97 H 6.71
(240.3) Found: C 80.11 H 6.94.

4-Methyl-4-aza-tricyclo[7.6.0.0^{3,7}]pentadeca-1(9),3(7),5-triene-2,8-dione (6)

According to the general procedure, 500 mg (1.59 mmol) of **2** and 258 mg (2.39 mmol) of **4** gave a crude product which was oxidized with 8.75 g (15.9 mmol) of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Chromatography furnished 110 mg (28%) of **6** as orange crystals (*m.p.* 126–128 °C). – $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ/ppm = 6.75, 6.54 (2 d, J/Hz = 2.5 each, 1H each, =CH), 3.97 (s, 3H, NMe), 2.67 (m, 4H, 2CH₂), 1.67–1.61, 1.50–1.46 (2 m, 4H each, 4CH₂). – $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ/ppm = 182.6, 178.3 (2 s, C=O), 145.2, 144.5, 129.6, 126.8 (4 s, quinone-C), 129.8, 106.9 (2 d, =CH), 36.3 (q, Me), 30.0, *26.68, 26.65, 24.8, 24.5 (5 t, CH₂); *signal has double intensity. – IR (KBr): ν/cm^{-1} = 3020, 2950, 2910, 2850 (=C–H, C–H), 1660 (C=O), 1625, 1610 (C=C).

$\text{C}_{15}\text{H}_{17}\text{NO}_2$ Calcd.: C 73.05 H 7.04 N 5.76
(243.3) Found: C 73.60 H 7.33 N 5.59.

4-Thia-tricyclo[7.6.0.0^{3,7}]pentadeca-1(9),3(7),5-triene-2,8-dione (7)

According to the general procedure, 636 mg (2.00 mmol) of **3** and 325 mg (3.00 mmol) of **4** gave a crude product which was oxidized with 11.0 g (20.0 mmol) of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Chromatography furnished 277 mg (56%) of **7** as yellow crystals (*m.p.* 106–107 °C). – $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ/ppm = 7.59, 7.52 (2 d, J/Hz = 5 each, 1H each, =CH), 2.75 (m, 4H, 2CH₂), 1.73–1.62, 1.53–1.47 (2 m, 4H each, 4CH₂). – $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ/ppm = 181.1, 179.7 (2 s, C=O), 146.6, 146.0, 143.3, 141.4 (4 s, quinone-C), 132.6, 126.2 (2 d, =CH), 29.97, 29.93, 26.6, *24.99, 24.94 (5 t, CH₂); *signal has double intensity. – IR (KBr): ν/cm^{-1} = 2960, 2935, 2910, 2850 (=C–H, C–H), 1650 (C=O), 1605 (C=C).

$\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$ Calcd.: C 68.26 H 5.73 S 13.02
(246.3) Found: C 68.42 H 5.84 S 12.48.

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