

Oxocarbons and related compounds. Part 25.¹ Heterocycle-fused benzocyclobutenediones. Synthesis of indolo-, benzofuro- and benzothieno-dihydrobenzocyclobutenediones and benzocyclobutenediones

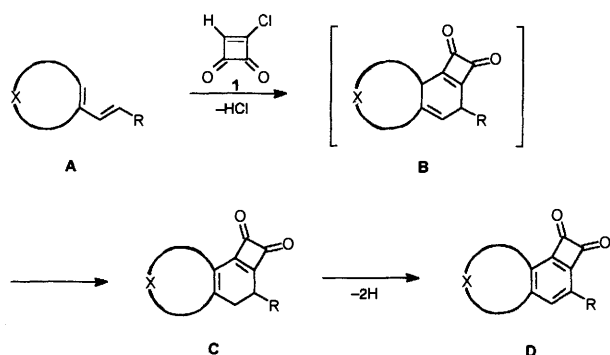
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A general and efficient procedure has been described for the synthesis of heterocycle-fused dihydrobenzocyclobutenediones and benzocyclobutenediones by reacting (alk-1-enyl)heterocycles with semisquaric chloride.

Substituted cyclobutenediones² and benzocyclobutenediones^{2f} have recently attracted much attention as synthons as well as in the construction of complex organic molecules.^{3,4} By contrast, only a small number of carbocycle-fused benzocyclobutenediones⁵ (CBBDS)^{5j,6} have been presented in the literature and, to the best of our knowledge, only one heterocycle-fused benzocyclobutenedione (HBBD) has been reported.⁷

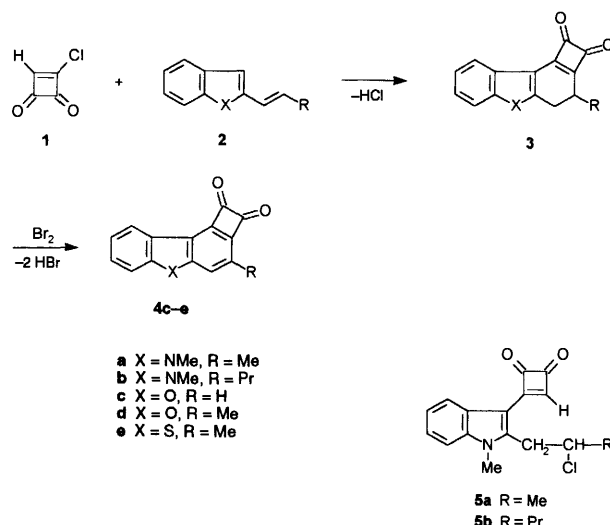
Recently^{5j} we have reported that (alk-1-enyl)arenes readily undergo Diels–Alder reactions with 3-chlorocyclobut-3-ene-1,2-dione (semisquaric chloride) **1**⁸ to give dihydrocyclobuta[*a*]naphthalene-1,2-diones, which were subsequently dehydrogenated to cyclobuta[*a*]naphthalene-1,2-diones. For potentially wider applicability, we have now extended this procedure, developing a simple, straightforward synthesis of the heterocycle-fused dihydrobenzocyclobutenediones **C** (Scheme 1). This involves the Diels–Alder reaction of an (alk-1-enyl)hetero-



Scheme 1

cyclic compound **A**, containing a conjugated diene system, with semisquaric chloride **1**, followed by regioselective elimination of hydrogen chloride to give **B** and subsequent allylic rearrangement to furnish **C**. Dehydrogenation of **C** should then afford the desired heterocycle-fused benzocyclobutenedione **D**.

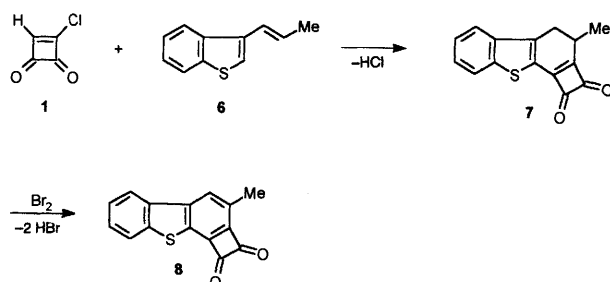
When the 2-(alk-1-enyl)-*N*-methylindoles **2a** and **2b** were heated with semisquaric chloride **1** in dichloromethane, the corresponding dihydrocyclobuta[*c*]carbazole-1,2-diones **3a** and **3b** were isolated from the reaction mixture by column chromatography (Scheme 2). In addition a chlorine-containing



Scheme 2 Synthesis of heterocycle-fused dihydrobenzocyclobutenediones and benzocyclobutenediones. For conditions see Table 1.

side-product was obtained in each case. The structures **5a** and **5b** were attributed to these. Similarly, the 2-(alk-1-enyl)-1-benzofurans **2c**, **2d** and 2-(prop-1-enyl)-1-benzothiophene **2e** reacted with semisquaric chloride **1** to give the benzofuro- and benzothieno-fused dihydrobenzocyclobutenediones **3c**, **3d** and **3e**, respectively (Scheme 2, Table 1).

In addition, 3-(prop-1-enyl)-1-benzothiophene **6** was also treated with semisquaric chloride **1** to give **7**, an isomer of **3e** (Scheme 3). The heterocycle-fused dihydrobenzocyclo-



Scheme 3 Synthesis of 3-methyl-3,4-dihydrobenzo[*b*]cyclobuta[*e*][1]-benzothiophene-1,2-dione and its dehydrogenation. For conditions see Table 1.

butenediones **3c**, **3d**, **3e** and **7** were easily dehydrogenated by treatment with bromine (*ca.* 1 equiv.) in boiling tetrachloromethane. The benzofuro- and benzothieno-fused benzocyclobutenediones **4c**, **4d**, **4e** and **8** thus obtained, are the first representatives of this class of compounds (Schemes 2 and 3).

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Table 1 Indolo-, benzofuro- and benzothieno-fused dihydrobenzocyclobutenediones and benzocyclobutenediones

Substrate	Solvent	Conditions (temp., t/h)	Product ^a	Yield ^b (%)	Mp ^c (T/°C)
2a	CH ₂ Cl ₂	rt, 20 h; then reflux, 1 h	3a	67	249–251
2b	CH ₂ Cl ₂	rt, 20 h; then reflux, 1 h	3b	30	177–178
2c	CH ₂ Cl ₂	rt, 48 h; then 60 °C, 0.5 h	3c	38	188–190 (decomp.)
2d	Neat	rt, 1 h; then 40 °C, 1 h; then 60 °C, 1.5 h	3d	45	176–178 (decomp.)
2e	CH ₂ Cl ₂	rt, 20 h; then reflux, 1 h	3e	35	167–168 (decomp.)
6	CH ₂ Cl ₂	rt, 24 h; then reflux, 1 h	7	56	205–207 (decomp.)
3c	CCl ₄	reflux, 5 h	4c	76	218–220 (decomp.)
3d	CCl ₄	reflux, 5 h	4d	59	198–200 (decomp.)
3e	CCl ₄	reflux, 4 h	4e	51	219–220
7	CCl ₄	reflux, 5.5 h	8	88	253–255

^a All compounds gave satisfactory elemental analyses and were characterized by IR, ¹H NMR, ¹³C NMR and mass spectroscopy. ^b Yields are of purified products. ^c Uncorrected.

Experimental

3-Methyl-3,4-dihydrobenzo[*b*]cyclobuta[*e*][1]benzofuran-1,2-dione 3d

Typical procedure. Semisquaric chloride **1** (1.16 g, 10 mmol) and 2-(prop-1-enyl)-1-benzofuran **2d** (1.58 g, 10 mmol; corrected for (*E*)-**2d**: 1.30 g, 8.23 mmol) were combined, and the mixture was stirred at rt for 60 min during which time the reaction mixture took on a dark-red colour. It was then heated at 40 °C for 1 h, and at 60 °C for 1.5 h. Liberated HCl was removed under reduced pressure. The resulting dark brown crystals were triturated with ethanol. The yellow crystals obtained were recrystallized from ethanol to give **3d** (0.88 g, 45%), mp 176–178 °C (decomp.) (Found: C, 75.6; H, 4.3. C₁₅H₁₀O₃ requires C, 75.6; H, 4.2); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2960, 1780–1760, 1600, 1545, 1160 and 765; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.50 (3 H, d, *J* 7.3 ‡), 2.95 (1 H, dd, *J* 8.6 and 18.6), 3.40 (1 H, dd, *J* 9.9 and 18.5), 3.62 (1 H, m), 7.30 (2 H, m), 7.48 (1 H, m) and 7.76 (1 H, m); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3)$ 18.1, 29.7, 30.7, 109.5, 111.8, 120.7, 122.4, 125.6, 155.9, 162.2, 189.1, 192.8, 193.1 and 196.1; *m/z* (EI) 238 (M⁺, 55%), 210 (M⁺ – CO, 49), 182 (M⁺ – 2CO, 79) and 181 (100).

3-Methylbenzo[*b*]cyclobuta[*e*][1]benzofuran-1,2-dione 4d

To a suspension of compound **3d** (0.48 g, 2.01 mmol) in CCl₄ (50 cm³) was added a solution of bromine (0.31 g, 1.91 mmol) in CCl₄ (20 cm³). The mixture was stirred and heated at reflux until no further HBr was generated (*ca.* 5 h). On cooling to –15 °C compound **4d** precipitated and it was filtered off and

recrystallized from ethanol to give yellow crystals (0.28 g, 59%), mp 198–200 °C (decomp.) (Found: C, 76.0; H, 3.6. C₁₅H₈O₃ requires C, 76.3; H, 3.4); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1780–1755, 1600, 1450, 1265, 1185, 1110 and 750; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.78 (3 H, s), 7.45 (1 H, t, *J* 7.6), 7.60 (3 H, m) and 8.17 (1 H, d, *J* 7.7); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3)$ 18.3, 112.3, 116.9, 119.7, 121.6, 123.3, 124.7, 129.5, 134.1, 157.4, 159.4, 167.3, 169.0, 193.2 and 193.7; *m/z* (EI) 236 (M⁺, 7%), 208 (M⁺ – CO, 19) and 180 (M⁺ – 2CO, 100).

Acknowledgements

The authors gratefully acknowledge financial support of this work from the Deutsche Forschungsgemeinschaft (DFG), Bonn-Bad Godesberg (Grant: Schm 309-6/1). They are also grateful to Dr G. Penzlin, Beilstein Institut, Frankfurt am Main, for his advice on nomenclature.

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‡ *J* Values given in Hz.

Paper 5/07573D
Received 20th November 1995
Accepted 11th January 1996