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A NEW AND CONVENIENT SYNTHESIS OF 1,2-DIOXOBENZOCYCLOBUTENE VIA PHOTODECARBONYLATION

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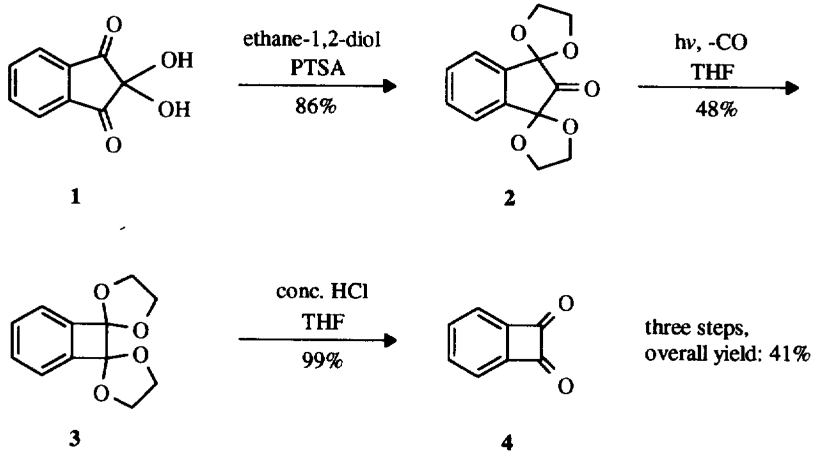
Abstract: The new preparation of 1,2-dioxobenzocyclobutene (**4**) via a short and efficient three-step route starting from the commercially available ninhydrin represents a superior procedure to all hitherto known syntheses of this valuable compound. The photo-extrusion of carbon monoxide from 1,3-bis(ethylendioxy)indan-2-one (**2**) is one of the rare examples using a decarbonylation of a five-membered cyclic ketone to prepare a highly strained and functionalized cyclobutane derivative. © 1997 Elsevier Science Ltd.

Since the first synthesis of 1,2-dioxobenzocyclobutene (**4**) by Cava et al.[1] in 1963 there has been continous interest in this compound up to now. The synthesis of indanone derivatives and naphthoquinones by Liebeskind, its use by Moore to synthesize natural products like nanaomycine D and deoxyfrenolycine or Krohn's enantioselective synthesis of daunomycinone derivatives are only a few examples of the high synthetic potential of **4**.[2]

Our new three step synthesis of 1,2-dioxobenzocyclobutene (**4**) starts from the commercially available ninhydrin (**1**) which is selectively protected with ethane-1,2-diol in 1,3-position to obtain 1,3-bis(ethylendioxy)indan-2-one (**2**) in 86% yield. This reaction succeeded despite Schönberg's fail in the late seventies.[3] The newly prepared **2**[4] was completely characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and correct combustion analysis. Up to now the photo-lability of 1,3-substituted indan-2-ones was mainly used in theoretical and spectroscopic studies.[5-9] However, the photolytic decarbonylation of **2** occurred in a smooth reaction during irradiation (pyrex immersion photochemical reactor with gas introduction, HPK 125 W Philips) for 5 h at 20°C in an argon atmosphere to give **3** in 48% yield. The final deprotection of 1,2-bis(ethylendioxy)benzocyclobutene (**3**) leads to the desired 1,2-dioxobenzocyclobutene (**4**) in quantitative yield.



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Although some synthetic routes to **4** are known nowadays[1,10-13] there are only the two five-step procedures by Liebeskind[14] and Schmidt,[15] which are commonly used for practical synthesis of **4**. In contrast to these our synthesis features several advantages: the short three step procedure uses only inexpensive and safe chemicals, is less time consuming, and its overall yield is even higher.

In addition, the two-step synthesis of 1,2-bis(ethylendioxy)benzocyclobutene (**3**) is a tremendous improvement on the way to the tricarbonylchromium(0) complex of **4**.[16] An example of its highly interesting chemistry is the possibility of this complex to undergo double anionic oxy-Cope rearrangements at -78 °C after addition of alkenyl lithium reagents.[16,17] It is now possible to synthesize this complex via **3** in a four-step (overall yield: 33%) instead of a eight-step procedure (overall yield: 20%, based on the Liebeskind synthesis of **4**).

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4. *1,3-Bis(ethylendioxy)indan-2-one* (**2**): A solution of **1** (20.0 g, 0.11 mol), ethane-1,2-diol (20.8 g, 0.34 mol), and a catalytic amount of PTSA (400 mg, 2 mmol) in 200 ml of benzene was refluxed for 72 h. The water produced in the reaction was removed azeotropically. The solvent was evaporated in vacuo and the crude product was purified by chromatography (diethyl ether). Evaporation of the solvent gave **2** as a colourless powder (23.6 g, 0.10 mmol, 86%) [mp. 115 °C(DSC)]. - IR (KBr): $\tilde{\nu}$ = 2973 (w) cm^{-1}, 2905 (w), 1777 (m, CO), 1330 (m), 1310 (m), 1029 (s, acetal-C-O), 945 (m), 765 (m), 740 (w). - ^1H-NMR (200.1 MHz, $CDCl_3$): $\delta = 4.28 + 4.39$ [m, 4H + 4H, 8(8',9,9')-H], 7.57 (s, 4H, arom. H). -^{13}C-NMR (50.3 MHz, $CDCl_3$): $\delta = 66.5$ [+, C-8(8') or C-9(9')], 66.6 [+, C-8(8') or C-9(9')], 101.4 [+, C-1(3)], 124.8 [-, C-4(7)], 132.0 [-, C-5(6)], 138.5 [+, C-3a(7a)], 209.4 (+, C-2). - MS (70 eV, 20 °C): *m/z* (%) = 248 (2) [M^+], 220 (34) [M^+ - CO], 148 (100), 133 (18), 104 (51).
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