Synthesis of 1,2-Diphenylcyclobutene-3,4-dione

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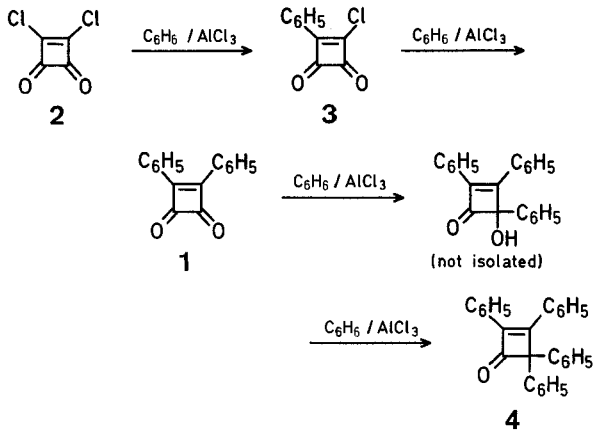
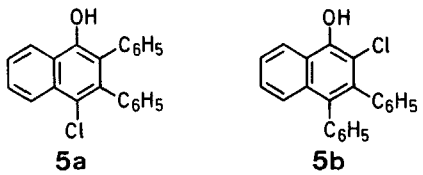
Several synthetic routes to 1,2-diphenylcyclobutene-3,4-dione (**1**) are known. Thus, perfluorocyclobutene is converted with phenyllithium to 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene, which may be hydrolyzed to **1** in sulfuric acid medium[1]. Benzene adds to 1-phenylcyclobutene-3,4-dione, forming 1,4-diphenyl-2-hydroxycyclobuten-3-one[2] and, thence, by action of diazomethane, 1,4-diphenyl-2-methoxycyclobuten-3-one[3]; the latter undergoes dehydrogenation to **1** in the presence of bromine[3]. Direct dehydrogenation of 1,4-diphenyl-2-hydroxycyclobuten-3-one to give **1** has also been observed[2]. Bromination of 1-phenylcyclobutene-3,4-dione leads to 1-phenyl-2-bromocyclobutene-3,4-dione[4], which is converted to **1** by reaction with benzene in the presence of aluminum chloride[2].

The last-named reaction step involving 1-phenyl-2-bromocyclobutene-3,4-dione can formally be regarded as a Friedel-Crafts type acylation of benzene, as the bromo substituent in this compound is attached to a vinylogous system and so shows the reactivity expected for an acyl halide[4]. It is, therefore, surprising that the direct route **2**→**3**→**1** involving reaction of the readily accessible[5] squaryl dichloride (**2**, 1,2-dichlorocyclobutene-3,4-dione) with benzene under Friedel-Crafts conditions has not been described in the literature, although the feasibility of this process was indicated in a

review article[6], and a later communication[5] mentioned, without details, the successful execution of step **2**→**3** (64% yield) in the presence of equimolar amounts of aluminium chloride.



We now wish to report that the aluminum chloride-catalyzed acylation of benzene with squaryl dichloride (**2**) proceeds smoothly to the stage of **1** (~80%) when **2** is treated with 2–3 moles of the Lewis acid in benzene solution at temperatures not exceeding ~10°. The dione **1**, separated in our work from the hydrolyzed reaction product by chromatography on silica gel and purified by recrystallization or vacuum sublimation, was identified by its m.p. and I.R. spectrum. Two preceding bands of the chromatogram furnished in low yield (1%) the previously described tetraphenylcyclobutenone (**4**) and a few mg (0.4%) of a compound to which we assign one of the isomeric naphthol structures **5**. While **4** most probably resulted from an addition-substitution reaction at one of the carbonyl C-atoms of **1**, the formation of **5** can reasonably be accounted for by (thermal) electrocyclic ring-opening of the respective chlorotriphenylcyclobutenone precursor (3-chloro-1,2,3-triphenylcyclobuten-4-one in the case of **5a**, 1-chloro-2,3,3-triphenylcyclobuten-4-one in the case of **5b**; although not isolated in this work, both compounds may conceivably arise in intermediary reaction stages) and subsequent intramolecular cycloaddition of the resulting ketene.



1,2-Diphenylcyclobutene-3,4-dione (1):
To the stirred solution of freshly sublimed squaryl dichloride (**2**; 0.40 g, 2.65 mmol) in dry benzene (10 ml), precooled to 10°, was added sublimed aluminum chloride (0.80 g, 6.0 mmol) under a blanket of dry nitrogen. The orange-brown mixture was stirred for 26 h at 10±1° under nitrogen with moisture protection. Following the addition of benzene (100 ml), the reaction mixture was treated with an equal volume of cold (0°) 0.1 *M* hydrochloric acid for complex decomposition. The separated organic phase, washed with water and dried with sodium sulfate, was evaporated to dryness under reduced pressure. Chromatography of the residue on silica gel (Merck type 7734, 125 g) with benzene/hexane (1:2 by vol) eluent produced two narrow bands, containing 0.005 g of crude **5** (first band) and 0.012 g of crude **4** (second band). Continued elution with benzene/hexane (1:1) furnished a broad yellow band containing 0.525 g of crude **1**. (Acetone elution of the remaining chromatogram gave a very small quantity of a mixture of polar products not further investigated.) Eluate separation was monitored throughout by T.L.C. on silica gel.

Compound **1** was recrystallized from hexane/chloroform: yield: 0.490 g (79%); m.p. 94–95° (Ref.[1,2]: m.p. 97–97.2°; 98°).

I.R. (KBr): ν_{CO} = 1782, 1770 cm^{-1}. Spectrum identical with that of authentic[1] **1**.

Mass Spectrum: m/e = 234 (M^+).

Compound **4** was purified by recrystallization from hexane: yield: 0.009 g (1.1%); m.p. 130–131° (Ref.[7]: m.p. 139°), undepressed on admixture of authentic **4** (m.p. 129–130°) prepared by a described[7] procedure.

$C_{28}H_{20}O$	calc.	C 90.28	H 5.42
(372.4)	found	89.84	5.58

I.R. (KBr): ν_{CO} = 1750 cm^{-1} (Ref.[7]: 1755 cm^{-1}).

Mass Spectrum: m/e = 372 (M^+).

The oxime of **4** formed colorless needles; m.p. 165–167° (from chloroform/hexane).

$C_{28}H_{21}NO$	calc.	N 3.62
(387.5)	found	3.91

Mass Spectrum: m/e = 387 (M^+).

Compound **5** was recrystallized from hexane; yield: 0.003 g (0.4%); colorless needles, m.p. 150–153° (purity not optimized).

$C_{22}H_{15}ClO$	calc.	C 79.85	H 4.57
(330.8)	found	78.40	4.69

I.R. (KBr): ν_{OH} = 3508 cm^{-1} (sh 3480 cm^{-1}).

Mass Spectrum: m/e = 330 (M^+).

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