An Improved Synthesis of Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane

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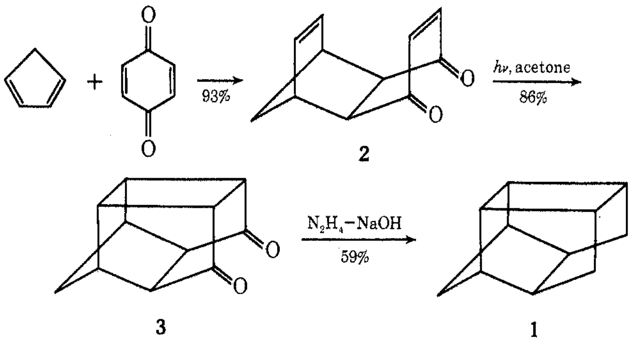
In connection with a study of the chemistry of strained hydrocarbons, it became necessary for us to synthesize the title compound, **1**. A six-step synthesis which affords **1** in *ca.* 14% overall yield has been reported by Stedman and coworkers.[1] In the present paper, we report an improved, three-step synthesis in which **1** is produced in 47% overall yield.

Our improved synthesis is shown in Scheme I. Diels–Alder addition of *p*-benzoquinone to cyclopentadiene has been reported[2] to afford the endo adduct **2** in high yield. Photochemical cyclization of **2** to **3** has likewise been reported to proceed smoothly.[3] We employed Wolff–Kishner reduction of diketone **3** to prepare **1**. Along with **1**, the reduction of **3** also afforded an unidentified olefin which could be readily separated from **1** by treatment of the crude reduction product with a solution of bromine in carbon tetrachloride, followed by elution chromatography.

Scheme I



The nmr and mass spectra of **1** have been discussed by Stedman.[1] Compound **1** is highly volatile, and precautions must accordingly be taken to minimize losses during its isolation.

Experimental Section

Melting points are uncorrected. Spectra were determined with the following instruments: Varian T-60 nmr spectrometer (TMS internal standard); Perkin-Elmer Model IR-8 infrared spectrophotometer; Hitachi Perkin-Elmer Model RMU-6E mass spectrometer (70 eV).

1,4,4a,8a-Tetrahydro-*endo*-1,4-methanonaphthalene-5,8-dione (2). To a solution of *p*-benzoquinone (243 g, 2.25 mol) in methanol (400 ml) at −70° was added a solution of freshly cracked cyclopentadiene (149 g, 2.27 mol) in cold methanol (100 ml). The solution was allowed to warm to room temperature, and the product was collected by suction filtration. Yellow-brown crystals (392 g, 93%) were obtained: mp 76.0–78.5° (lit. mp 75.8–76.2°,[4] 77–78°[5]); nmr ($CDCl_3$) δ 1.48 (m, 2 H, methylene bridge), 3.28 (m, 2 H, 4a, 8a protons), 3.52 (m, 2 H, bridgehead protons), 6.02 (m, 2 H, ethylene bridge protons), 6.52 (s, 2 H, enone vinyl protons); ir (KBr) 3320 (w), 1660 (vs, C=O), 1601 (s, conjugated C=C), 1295 (m), 1280 (m), 1060 (m), 875 (m), and 720 cm^{-1} (m).

Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (3). A solution of **2** (40 g, 0.23 mol) in ethyl acetate (500 ml) was irradiated for 12 hr with a Hanovia medium-pressure Hg lamp (Pyrex filter). The solution was concentrated, whereupon **3** crystallized as a colorless, microcrystalline solid (34.5 g, 86%): mp 243.0–243.5° (lit.[3] mp 245°); nmr ($CDCl_3$) AB pattern, J = 12 Hz, δ_A 1.86, δ_B 2.10 (2 H, methylene bridge protons), broad envelope, δ 2.5–3.3 (8 H); ir (KBr) 2990 (s), 2930 (m), 2870 (m), 1742 (vs, C=O), 1720 (vs, C=O), 1185 (m), 1055 (s), 855 (m), and 720 cm^{-1} (m).

Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (1). A solution of **3** (2.0 g, 11.5 mmol), 95% hydrazine (4 ml), and sodium hydroxide (1 g) in diethylene glycol (55 ml) was heated at 160–200° for 3 hr. The cooled reaction mixture was extracted with pentane (100 ml) and the pentane extracts were dried (Na_2SO_4). The crude product was found to contain an unidentified olefinic impurity. The filtered pentane solution was treated with excess 5% Br_2–CCl_4 solution, and the resulting product was chromatographed on neutral alumina (pentane eluent). Compound **1** was obtained as a colorless, waxy solid (990 mg, 59%): mp 204.0–204.5° (sealed tube) (lit.[1] mp 207–208°); nmr ($CDCl_3$) AB pattern, J = 12 Hz, δ_A 0.98 (br d), δ_B 1.16 (d) (4 H, 8- and 11-CH_2), AB pattern, J = 10 Hz, δ_A 1.30, δ_B 1.63 (2 H, 4-CH_2), δ 2.21 (envelope, 4 H, CH), and δ 2.55 (envelope, 4 H, CH); ir (KBr) 2950 (m), 2860 (s), 1460–1430 (w), and 1320–1270 cm^{-1} (w); mass spectrum m/e 146 (molecular ion), 131, 117, 91, and 80 (base peak).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.66; H, 9.55.

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Registry No.—**1**, 4421-32-3; **2**, 51175-59-8; **3**, 2958-72-7; *p*-benzoquinone, 106-51-4; cyclopentadiene, 542-92-7.

References and Notes

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Reaction of 4-Nitrobenzil with Cyanide Ion in Aprotic Solvents

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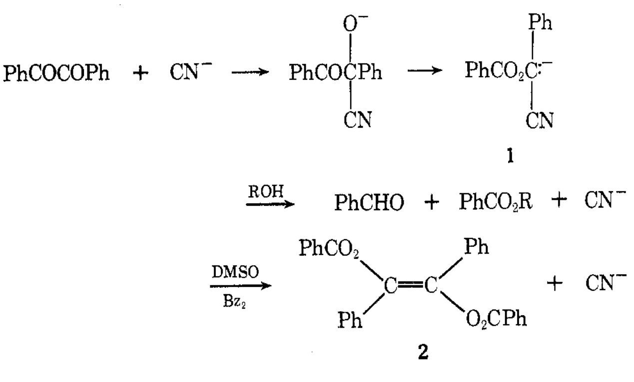
The reaction of benzil with cyanide ion has been shown to proceed differently in alcoholic solvents[1] than in dimethyl sulfoxide (DMSO).[2] The products in alcohol are benzaldehyde and the corresponding benzoate ester, whereas in DMSO the sole product is *trans*-α,α'-stilbenediol dibenzoate (**2**). The proposed mechanism for the reaction in both solvent systems (Scheme I) assumes cleavage of the central C-C bond in benzil by cyanide ion to form resonance-stabilized carbanion **1**. Reaction of **1** with *solvent* in the alcoholic systems leads to products, whereas in the absence of proton donor, *e.g.*, in DMSO, **1** is forced to attack a second benzil molecule with the formation of **2**.

More recently, Schowen and Kuebrich[3] evaluated the usefulness of **1**, generated from benzil and cyanide ion in

Scheme I



$$PhCOCOPh + CN^- \longrightarrow PhCO\overset{O^-}{\underset{CN}{C}}Ph \longrightarrow PhCO_2\overset{Ph}{\underset{CN}{C}}{:}^-$$

1

$$\xrightarrow{ROH} PhCHO + PhCO_2R + CN^-$$

$$\xrightarrow[Bz_2]{DMSO} (PhCO_2)(Ph)C{=}C(Ph)(O_2CPh) + CN^-$$

2