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 reported² 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.





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 93%) were obtained: mp 76.0-78.5° (lit. mp 75.8-76.2°,4 77g, 93%) were obtained: mp 70.0-70.0 (nt. mp 70.0-70.2 , $78^{\circ}5$); nmr (CDCl₃) δ 1.48 (m, 2 H, methylene bridge), 3.28 (m, 2 H, 1.48° (m, 2 H, 1.48° 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 so-

lution 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° a coloriess, microcrystalline solid (34.5 g, 80%): mp 240.0-245.5 (lit.³ mp 245°); nmr (CDCl₃) 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 (Na₂SO₄). The crude product was found to contain an unidentified olefinic impurity. The filtered pentane solution was treated with excess 5% Br₂-CCl₄ 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 (CDCl₃) AB pattern, J = 12 Hz, δ_A 0.98 (br d), $\delta_{\rm B}$ 1.16 (d) (4 H, 8- and 11-CH₂), AB pattern, J = 10 Hz, δ_A 1.30, δ_B 1.63 (2 H, 4-CH₂), 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 C11H14: 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.

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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 solvents¹ 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 Kuebrich³ evaluated the usefulness of 1, generated from benzil and cyanide ion in



several solvent combinations, as a model for "active aldehyde" intermediates in (a) the benzoin condensation and (b) thiamine action in biological systems. This research group^{3,4} demonstrated that 1, generated in the presence of a variety of added electrophiles, gave rise to a spectrum of products.

While in all instances¹⁻⁴ the products obtained from the benzil-cyanide reaction has been logically accounted for by invoking the intermediacy of 1, the intermediate, per se, has not been isolated. In any mechanistic study, the trapping or otherwise isolation of a proposed intermediate is considered of value in the compilation of data which allows for eventual elucidation of the reaction path. As an extension of our earlier work,² this report notes the isolation of the nitro derivative of intermediate 1, 4-nitromandelonitrile benzoate (3), in good yield from the reaction of 4-nitrobenzil with cvanide in DMSO or N.N-dimethylformamide (DMF). The reaction is shown in eq 1. In no ex-

$$O_{2}NPhCOCOPh \xrightarrow{CN} O_{2}NPhC \xrightarrow{} O_{2}NPhC \xrightarrow{} H^{+}-H_{2}O \xrightarrow{} O_{2}CPh \xrightarrow{} O_$$

periment was the corresponding stilbenediol dibenzoate detected. Thus, the role of cyanide ion is now one of reactant in contrast to that of catalyst in the reaction with benzil.

These results are of added interest in view of the findings of Kwart and Baevsky¹ that 4-nitrobenzil and cyanide ion are unreactive in alcoholic solution. These investigators observed the formation of a stable, colored solution which readily reverted to starting material. The generation of a stable semiguinone was considered a possibility. It seems reasonable, in view of our findings, that an alternate explanation can be offered. Thus, the reaction might have failed owing to the relatively low ratio (implied, though not stated¹) of cyanide catalyst to 4-nitrobenzil. Perhaps cyanide was simply consumed to form trace amounts of 4.

The success of the reaction in aprotic solvents presumably results from the inertness of 4 toward another molecule of 4-nitrobenzil. The negative charge is more completely delocalized in 4 (relative to 1) owing to the favorable location of the nitro substituent.

The obvious analogy is drawn between the benzil-cyanide reaction and the benzoin condensation where cyanide also acts both as the nucleophile and as a group which delocalizes the negative charge on the intermediate carbanion.⁵ The analogy is extended in that, while 4-nitrobenzaldehyde readily undergoes cyanohydrin formation,⁶ it fails in the benzoin condensation.⁷ As in our reaction, the best explanation seems to be that the delocalizing influence of the nitro group renders the intermediate so inert as to react no further with starting material.

Identification of 3 was accomplished by spectral analysis and comparison with a sample of benzoylated 4-nitromandelonitrile. It is interesting that C = N absorption, in the 2100-2400-cm⁻¹ region of the ir spectrum, is absent. However, this observation is in agreement with an earlier report that the C = N stretch in compounds where the cyano group is attached to oxygenated carbon is 'quenched" to the point of being extremely weak or not observable at all.8

Experimental Section⁹

Starting Materials. 4-Nitrobenzil was prepared according to the method of Womack, Campbell, and Dodd.10 The solvents, DMSO and DMF, were distilled from calcium hydride at reduced pressure. Other materials were available in reagent grade and were used without further purification.

4-Nitrobenzil and Sodium Cyanide in DMSO. Sodium cyanide (0.25 g, 5.1 mmol) was stirred into 40 ml of solvent under an atmosphere of nitrogen. 4-Nitrobenzil (1.28 g, 5.0 mmol) was added in a single portion at room temperature. The solution at once turned deep violet in color. After 1.5 min, the reaction mixture was poured into an acidified ice-water slurry. The resulting suspension was extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and evaporated. The residue (red-brown oil) was triturated with ethanol to afford light yellow crystals (0.82 g, 58%) of 4-nitromandelonitrile benzoate (3), mp 112-114° (ethanol).

Anal. Calcd for C15H10N2O4: C, 63.83; H, 3.54; N, 9.93. Found: C, 63.80; H, 3.69; N, 10.07.

The nmr spectrum showed a 1 H singlet (methinyl) at δ 6.9 and a 9 H multiplet at δ 7.5-8.5 (aromatic). The ir spectrum showed carbonyl absorption at 1725 cm⁻¹. No absorption for C=N was observed.⁸ The mass spectrum (30 eV) showed m/e (rel intensity) 282 (M^+), 255 (8), 106 (46), 77 (100), m* 230.6.

4-Nitromandelonitrile Benzoate (3). The procedure used by Cronyn¹¹ for the preparation of 3-nitromandelonitrile benzoate was adopted. A suspension was prepared in an ice bath from 4nitrobenzaldehyde (3.77 g, 25 mmol) and 5 ml of water, to which was added benzoyl chloride (3.64 g, 25.8 mmol). Potassium cyanide (2.0 g, 31.5 mmol) in 3 ml of water was added in one portion with stirring. The resulting yellow crystals were filtered and triturated with ethanol to afford the crude product (5.0 g, 70.8%, mp 108-111°). Recrystallization from ethanol resulted in an almost colorless sample, mp 114-115°. The material was identical with 3 in the previous experiment as shown by mixture melting point and comparison of spectral data.

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Registry No.-3, 51130-02-0; 4-nitrobenzil, 22711-24-6; NaCN, $143 - 3\overline{3} - 9$.

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Synthesis of Alkanesulfonyl Isocyanates by Thermolysis of Trimethylsilylated Sulfonyl Carbamates

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A communication by Greber and Krideldorf¹ describing the thermolysis of N-silylated carbamoyl chlorides, anhy-