Ar CH, Ar CH_2 and CH_2); uv max (95% C_2H_5OH) 256 mμ (ε 2280), 267 (1935), and 274 (1950).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.32; H, 8.67.

Dimer **7**, isolated from the mixture by preparative gas chromatography (UC W-98 on acid-washed Gas-Pack W), was a viscous liquid: bp 180° (0.2 mm); ir (film) 3000, 2900, 2820, 1480, 1450, 1430, 1040, 1020, 806, 767, 737 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 260 (51), 131 (63), 130 (62), 129 (100), 128 (74), 115 (43), and 104 (69); nmr (CCl_4) δ 6.97 (m, 8, Ar H), 5.83 (t, 1, vinyl), 3.2–2.45 (m, 6, Ar CH_2), 2.4–1.4 (overlapping m, 5, Ar CH_2CH_2 and >C=CHCH); uv max (95% C_2H_5OH) 202 mμ (ε 10,100) and 268 (5500).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.90.

Synthesis of 1,2′-Binaphthyl (9) by Dehydrogenation of C_{20} Dimers.—The dimer fraction (4.3 g of **5**, **6**, and **7**) was mixed with 10% Pd/C (0.5 g) in a 50-ml one-neck flask equipped with reflux condenser and gas outlet tube. As the flask was lowered into a preheated (350°) Woods metal bath, vigorous evolution of gas occurred. After 10 min, gas evolution had subsided, but heating was continued for 1 hr. After cooling, the residue was dissolved in petroleum ether,[6a] filtered, and concentrated to give 4.0 g of viscous yellow oil. The latter was distilled [153–158° (0.02 mm)] to give 3.9 g (92%) of light yellow solid. This constitutes a 57% yield of **9** based on the amount of reacted naphthalene. After elution through alumina and silica gel with petroleum ether,[6a] followed by concentration of the solution, a white solid was obtained: mp 76.5–77.5° (lit.[7] mp 76°); mmp with **9** prepared from **8**,[3c] 76–77°; mass spectrum (70 eV) *m/e* (rel intensity) 254 (100), 253 (72), 252 (53), 250 (13), 127 (10), 126 (27); nmr ($CDCl_3$) δ 7.18–8.05 (m).

Reduction of 5 with Sodium and Diethylamine.—To 6.5 g (0.025 mol) of **5** in 250 ml of diethylamine was added 2.3 g (0.1 g-atom) of Na over a period of several hours. A dark brown color developed in less than 1 min and persisted throughout the reaction time of 22 hr. The reaction mixture was quenched in ice and extracted with ether, and the ether solution was extracted with 10% HCl.

The ether remaining after washing with water was dried (Na_2SO_4) and concentrated to give 5.8 g of hydrocarbons. The acidic and aqueous extracts were combined, made basic with NaOH and extracted with ether, dried (Na_2SO_4), and concentrated to give 0.7 g of nonvolatile amines.

The hydrocarbon fraction showed a trace of **6** and **7**, 10% of **5**, and 89% of an undetermined mixture. When the latter (2.5 g) was treated as before with Pd/C (0.25 g) in 100 ml of refluxing toluene for 5 hr,[3c] a viscous oil (2.1 g) was obtained which showed the ratio **5**:**6**:**10** (62:1:37) by glc.[6b]

Isolation and Identification of 1′,2′,3′,4′,5,6,7,8-Octahydro-1,2′-binaphthyl (10).—The mixture from the preceding reduction was eluted with petroleum ether[6a] through a column of silica gel and basic, acidic, and neutral alumina. From the first fraction which eluted from the column, pure **10** was obtained: bp 175–180° (0.2 mm); ir (film) 2990, 2800, 2690, 1580, 1488, 1455, 1433, 772, 743, 716 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 262 (50), 131 (27), 130 (100), 129 (23), 115 (21), 104 (100); nmr (CCl_4) δ 6.96 (m, 7, Ar H), 3.30–2.45 (m, 9, Ar CH and Ar CH_2), 2.12–1.45 (m, 6, CH_2); uv max (95% C_2H_5OH) 258 mμ (ε 1208), 267 (1085), 274 (888).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.83; H, 8.40.

Catalytic Reduction of 5, 6, and 7.—A mixture (3.6 g) of **5**:**6**:**7** (32:9:9) was stirred (Teflon-covered magnet) at 25° in a 500-ml fluted flask with 0.4 g of 10% Pd/C and 150 ml of 95% ethanol. Hydrogen (1 atm) was introduced and after 5 days, **5** and **7** had disappeared. After filtration (Dicalite Filter-aid) and concentration, a viscous oil remained (3.2 g) which proved to be a mixture of **6**:**10** (62:38) by glc analysis.

Registry No.—**5**, 32675-22-2; **6**, 27426-98-8; **7**, 23439-78-3; **9**, 4325-74-0; **10**, 32675-26-6; naphthalene, 91-20-3.

Acknowledgments.—We are grateful to the American Petroleum Institute and the Research Foundation, Oklahoma State University, for their assistance. We thank Dr. O. C. Dermer for having read the manuscript.

(7) H. A. Weidlich, *Ber.*, **71B**, 1201 (1938).

On the Preparation of 1,4-Dicarboxycubane[1]

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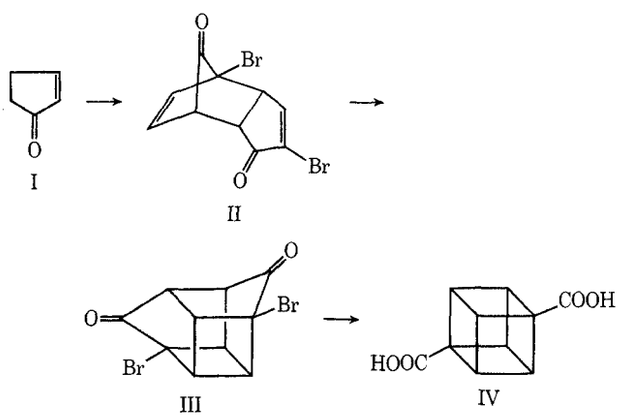
Received June 30, 1971

The synthesis of cubane and several important derivatives including the 1,4-diacid was reported in a communication in 1964.[2] Recently, Chapman and his associates[3] have reported a closely related alternative route, chosen because of difficulties encountered in their attempts to follow the preparative method outlined by Eaton and Cole[2] for the synthesis of 1,4-disubstituted cubanes. We wish to report that we have employed the original approach without difficulty. The procedures derive from those employed by Cole[4] and are described fully in the Experimental Section. We note in particular that the conversion of the caged dimer



III to 1,4-dicarboxycubane (IV) was accomplished with potassium hydroxide in 55% yield and with sodium hydroxide in 44 (first experiment), 70, 75, 78, and 72% yield, respectively.

Experimental Section

2-Cyclopentenone (I).—A mixture of cyclopentendiols (100 g, 1.0 mol) was converted to 2-cyclopentenone by the method of Depuy and Eilers.[5] A second fractionation of the initial product provided colorless 2-cyclopentenone (47 g, 57%, bp 151–154°).

2,4-Dibromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (II).—2-Cyclopentenone (50 g, 0.61 mol) was added to a slurry of *N*-bromosuccinimide (240 g, 1.45 mol) in carbon tetrachloride (700 ml). The reaction mixture was heated to reflux, stirred vigorously, and illuminated with a General Electric sun lamp to start the reaction. After the initial exothermic reaction had subsided, additional 2-cyclopentenone (50 g) was added. The solution was refluxed for 3 hr. The cooled reaction mixture was filtered and the filtrate was concentrated *in vacuo* at room temperature. The residue was dissolved in anhydrous ether (11.) previously saturated with lithium bromide (dried overnight at 100° *in vacuo*). The solution was cooled to −30°. Bromine (1.17 mol) was then added dropwise at a rate approximately equal to the reaction rate. The bath temperature was maintained at −30 to −35°. After the bromination reaction was complete,

(1) This research was supported by a grant from the National Science Foundation.

(2) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964).

(3) N. B. Chapman, J. M. Key, and K. J. Toyne, *J. Org. Chem.*, **35**, 3860 (1970).

(4) T. W. Cole, Jr., Dissertation, University of Chicago, 1966.

(5) C. H. Depuy and K. L. Eilers, *Org. Syn.*, **42**, 38 (1962).

methylene chloride (750 ml) was added slowly while the temperature was maintained at −25 to −30°. Triethylamine (228 g, 2.26 mol) was then added dropwise in 2.5 hr. During this addition the temperature was maintained at −20 to −30° for the first 90 min. The temperature was allowed to rise to −10° over the last hour. Further methylene chloride (about 250 ml) was added to aid stirring. When the addition was complete, water (1 l.) was added. The mixture was then filtered to collect the solids, and the organic and the aqueous layers of the filtrate were separated. The aqueous layer was extracted with methylene chloride. The filter cake was washed with hot methylene chloride six times. The combined organic layers were washed with hydrochloric acid (6 *M*, 300 ml) twice followed by brine (300 ml) twice. The organic phase was dried over magnesium sulfate. Removal of the solvent *in vacuo* yielded crude II (42 g). Recrystallization from ethyl acetate provided colorless needles of the product, mp 155–155.5°. The mother liquor (which contained a skin irritant) was refrigerated and a second batch of solid was obtained. This material was worked up to yield additional II (21 g). The overall yield was 33%. The spectroscopic properties of the product were identical with those reported by Eaton and Cole.[2]

6,10-Dibromopentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]deca-5,9-dione (III).—Dimer II (5 g, 15.7 mol) was dissolved in hot methanol (60 ml) and then cooled to room temperature. Methanolic hydrogen chloride (2 ml) was added. The mixture was transferred to a Pyrex irradiation cell with additional methanol (20 ml). The solution was irradiated with an Hanovia 450-W mercury lamp for 90 min. The solvent was removed *in vacuo*. The orange waxy solid was dissolved in benzene (300 ml) and the mixture was boiled to remove methanol. The hot benzene solution was passed through basic alumina (10 g) and the column was flushed with hot benzene. The solution was evaporated to dryness. The solid was dissolved in benzene (10 ml). *n*-Hexane was added dropwise to precipitate the product. Recrystallization from benzene yielded III (4.2 g, 84%, mp 228–230°). The product exhibited the spectroscopic properties reported by Eaton and Cole.[2]

1,4-Dicarboxycubane (IV).—In a typical experiment, compound III (5.0 g, 15.7 mmol) was added to sodium hydroxide solution (25%, 50 ml). The mixture was refluxed (110°) for 2 hr, then cooled to 0°. The solution was neutralized by the dropwise addition of cold concentrated hydrochloric acid. The temperature of the solution was kept near 0°. As the pH was reduced the solution changed from dark brown to light tan. The precipitation of the product appeared to be complete between pH and 1 and 3. Filtration yielded the desired product as a very light tan powder (2.3 g, 75%). Pure 1,4-dicarboxycubane, mp 226° dec, was obtained by recrystallization from acetic acid. The crude diacid (2.3 g, 11.9 mmol) was dissolved in methanol (50 ml) containing the hydrogen form of methanol washed Bio-Rad cation exchange resin AG 50w.-X8 (300 mg). The mixture was refluxed for 12 hr. The warm solution was filtered to collect the resin and 1,4-dicarbomethoxycubane (2.35 g, 90%, mp 161–162° after recrystallization from methanol) precipitated as the solution cooled.

Registry No.—II, 32846-64-3; III, 25867-85-0; IV, 32846-66-5.

Formation of an Unusual Dihydropyrazine Di-*N*-oxide during Hydrolysis of an α-Oximino Acetal

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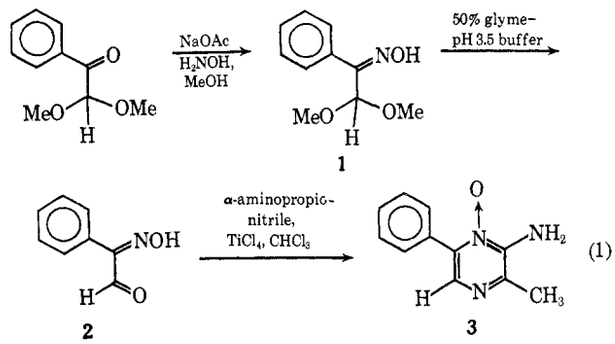
Received July 26, 1971

In connection with the synthesis and structural elucidation of *Cypridina* etioluciferamine,[1] certain model compounds were needed for the spectrographic information they would yield. The most important of these was 2-amino-3-methyl-6-phenylpyrazine 1-oxide (**3**) which was to be synthesized *via* the pathway shown in eq 1. It was therefore necessary to prepare the unknown phenylglyoxal 2-oxime **2**. The conversion of the known[2,3] phenylglyoxal acetal to a mixture of the *Z* and *E* isomers of **1** was accomplished in 93% yield by the conditions shown in eq 1.[4] The next step, the acid hydrolysis of an α-oximino acetal to the corresponding α-oximinoaldehyde (eq 2), is at face value a simple



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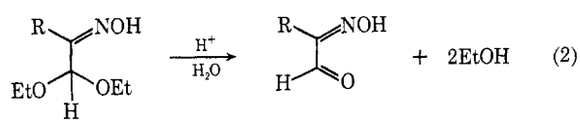

(2)

reaction. The yields in this type of conversion are reported to be good, and the desired product is easily isolable (R, yield: isobutyl, 63%;[5] *sec*-butyl, 64%;[6] methyl, 82%[6]). We therefore anticipated no difficulties in the conversion of **1** to **2**. Reaction conditions similar to those stated in the literature[5,6] were used for the hydrolysis of **1**. After the isolation and recrystallization procedure described in the Experimental Section, physical data on the colorless crystals obtained (71% yield) clearly indicated that this material was not the expected phenylglyoxal 2-oxime. The 100-MHz nmr spectrum (DMSO-d_6) of the compound isolated (Figure 1) shed considerable light on its structure. The singlet at τ 2.73 corresponds to the protons of a phenyl ring which is not directly attached to an electron-withdrawing center. The two multiplets at τ 1.60–1.85 and 2.42–2.64 represent phenyl ring protons which are separated due to a powerful electron-withdrawing element attached directly to that aromatic ring.[7] Furthermore, the two doublets at τ 2.21 and 3.84 and the doublet of doublets at τ 3.68 indicate an ABX spin

(1) T. P. Karpetsky and E. H. White, *J. Amer. Chem. Soc.*, **93**, 2333 (1971).

(2) W. Madelung and M. E. Oberwegner, *Justus Liebigs Ann. Chem.*, **490**, 232 (1931); *Chem. Abstr.*, **26**, 474 (1932).

(3) W. Madelung and M. E. Oberwegner, *Chem. Ber.*, **65B**, 936 (1932); *Chem. Abstr.*, **26**, 4584 (1932).

(4) The preparation of **1** was modeled after a method originally applied to isobutyrophenone: H. M. Kissman and J. Williams, *J. Amer. Chem. Soc.*, **72**, 5323 (1950).

(5) J. J. Gallagher, G. T. Newbold, W. Sharp, and F. S. Spring, *J. Chem. Soc.*, 4870 (1952).

(6) G. T. Newbold, W. Sharp, and F. S. Spring, *ibid.*, 2679 (1951).

(7) For example, we have found that the phenyl ring protons in 2-amino-3-methyl-6-phenylpyrazine 1-oxide (**3**) are separated into two multiplets at τ 2.10–2.28 and 2.45–2.63.