from an ethanol–acetone mixture: mp 74.0–74.5°; $[\alpha]_D$ +16.5° (*c* 5.07); ir (CS_2) 5.75 (C=O), 8.05, 9.78, 9.73 μ (acetate CO–); nmr τ 9.23, 9.08 (s, 6, 2 Me), 7.98 (s, 3, $-OOCCH_3$), 5.33 (m, 1, CHOAc).

Anal. Calcd for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found: C, 80.03; H, 11.25.

Registry No.—**1**, 1251-13-4; **2**, 40429-72-9; **4**, 35649-45-7; **5**, 2603-77-2; **9**, 40429-41-2; **10**, 40429-42-3; **11**, 1259-02-5; **15**, 5916-16-5; **16**, 40429-45-6; **17**, 40429-46-7; **18**, 19684-29-8; methanesulfonyl chloride, 124-63-0; acetic anhydride, 108-24-7.

Synthesis of 3,4,5,10,11,12-Cyclotetradecahexaene-1,8-dione, a Monocyclic Dicumulenedione[1]

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We have recently described the synthesis of 12- and 14-membered monocyclic diallenes containing carbonyl groups,[2] and we have explored this method as a means of preparing monocyclic dicumulenes. We now report the synthesis of 3,4,5,10,11,12-cyclotetradecahexaene-1,8-dione (**6**), and the attempted preparation of 3,4,5,6,11,12,13,14-cyclohexadecaoctaene-1,9-dione (**8b**).

The racemic diallene (**1**), prepared by the previously described method,[2] was treated in pentane at 0° with excess bromoform and potassium *tert*-butoxide. Two isomeric bis(dibromocarbene) adducts were obtained, **2a** (mp 117–118°) and **2b** (mp 95–97° dec). The spectra of **2a** and **2b** (Table I) both showed signals in the olefinic and cyclopropyl regions, but no signals in the allenic region (τ 4.5–5.5), and thus addition to both allene groups of **1** must have occurred. Furthermore, the nmr spectrum of **2a** showed only one type of methoxyl proton, which suggests that **2a** most probably has the symmetric structure shown.[3] By contrast, the nmr spectrum of **2b** showed two methoxyl signals, and the spectrum can be accommodated by a number of isomeric structures.

The *meso*-diallene **3**,[2] under the same conditions, gave two further bis(dibromocarbene) adducts, **4a** (mp 79–80° dec) and **4b** (mp 77–78° dec). The nmr spectra (Table I) showed that both allenic groups in **3** had reacted. The spectrum of **4b** had three types of methoxyl signals, suggesting the asymmetric structure shown,[4] whereas that of **4a** showed two methoxyl signals and consequently provided less structural information.

(1) For a preliminary communication of part of this work, see P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *Chem. Commun.*, 1018 (1971).

(2) P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *J. Amer. Chem. Soc.*, **95**, 4582 (1973).

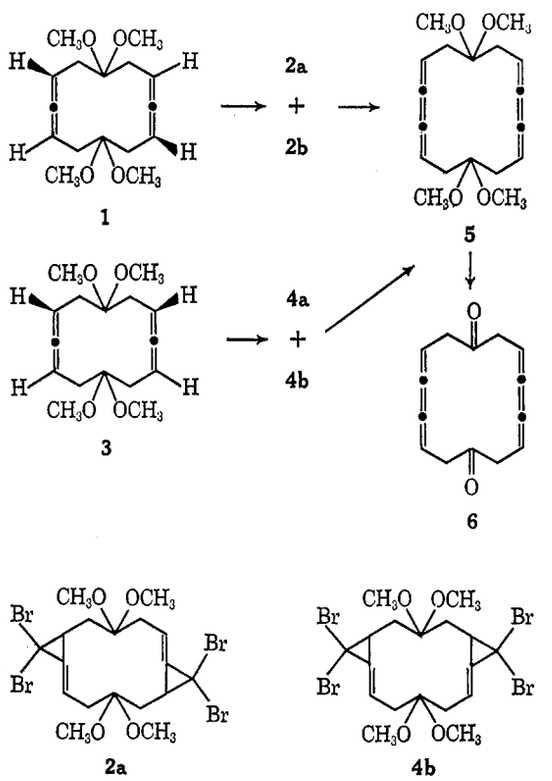
(3) The cyclopropyl rings in **2a** might be both on the same side of the 12-membered ring or on opposite sides. For either structure, the spectrum is still deceptively simple, since two methoxyl groups in different environments must have fortuitously coincidental chemical shifts. However, the environment of the methoxyl groups in the alternative isomers are even less similar.

(4) The two cyclopropyl rings would have to be on the same side of the 12-membered ring, and the spectrum is again deceptively simple.

TABLE I

NMR SPECTRA (100 MHz, CCl_4) OF **2a**, **2b**, **4a**, AND **4b** AS τ VALUES RELATIVE TO TMS

2a	3.74	(m, 2 H, olefin)
	6.72	(s, 12 H, OCH_3)
	7.32	(d, J = 8 Hz, 4 H, allylic CH_2)
	7.65	(d, J = 14 Hz, 2 H, CH_2)
	7.86	(d, J = 12 Hz, 2 H, CH_2)
	8.64	(dd, J = 12, 14 Hz, 2 H, cyclopropyl)
2b	3.66	(m, 2 H, olefin)
	6.66	(s, {12H, OCH_3})
	6.73	(s, {12H, OCH_3})
	7.26–8.00	(m, 8 H, allylic CH_2 + CH_2)
	8.32	(dd, J = 7, 14 Hz, 2 H, cyclopropyl)
4a	3.64	(m, J = 2, 8, 8 Hz, 2 H, olefin)
	6.70	(s, 6 H, OCH_3)
	6.77	(s, 6 H, OCH_3)
	7.32	(d, J = 8 Hz, 4 H, allylic CH_2)
	7.56	(d, J = 14 Hz, 2 H, CH_2)
	7.88	(dd, J = 2, 10 Hz, 2 H, CH_2)
	8.67	(dd, J = 10, 14 Hz, 2 H, cyclopropyl)
4b	3.63	(m, J = 2, 8 Hz, 2 H, olefin)
	6.64	(s, 3 H, OCH_3)
	6.74	(s, {9H, OCH_3})
	6.78	(s, {9H, OCH_3})
	7.30–7.70	(m, 4 H, allylic CH_2 + CH_2)
	8.38	(dd, J = 8, 16 Hz, 2 H, cyclopropyl)



When a mixture of the racemic **1** and *meso*-**3** diallenes were treated with bromoform and potassium *tert*-butoxide, a mixture of the four bis adducts was obtained. These could be separated by chromatography and this is the best method for the preparation of these compounds.

Reaction of either **2a** or **4a**, or a mixture of all four isomers, with methyllithium in ether at −10° gave a solution of the dicumulene **5**, which was stable under these conditions for several days. Removal of the ether below 0° gave **5** as a crystalline compound, which

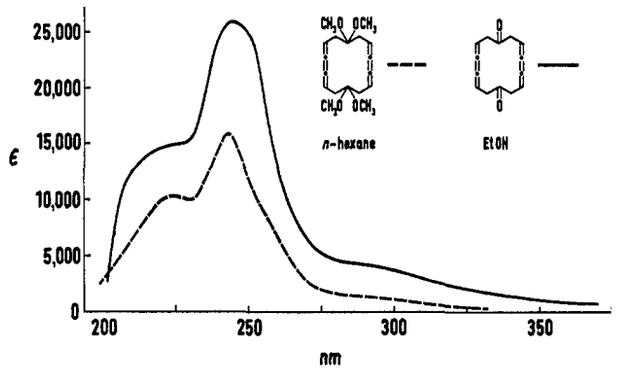


Figure 1.—Electronic spectra of **5** (in *n*-hexane) and **6** (in ethanol).

rapidly decomposed at higher temperatures, forming material insoluble in ether. The structure assigned to **5** is based on its spectral properties and ready hydrogenation (with concomitant hydrolysis) to 1,8-cyclotetradecanedione.[5] The nmr spectrum of **5** at 0° in CCl_4 showed signals at τ 4.85 (m, 4 H, cumulene), 6.82 (s, 12 H, methoxyl), and 7.52 (m, 8 H, methylene). The nmr spectrum was found to be temperature dependent, but irreversible changes occurred above 20°. The electronic spectrum [$\lambda_{max}^{n\text{-hexane}}$ 224 nm (ϵ 10,300), 243 (15,900), 290 sh (1350)][6] was consistent with the presence of the butatriene chromophore (Figure 1).[7]

Hydrolysis of the diketal **5** gave 3,4,5,10,11,12-cyclotetradecahexaene-1,8-dione (**6**) in 75% yield as a crystalline solid, mp ~130° dec. The monocyclic nature of **6** was confirmed by hydrogenation to 1,8-cyclotetradecanedione. The nmr spectrum ($CDCl_3$) of **6** showed signals at τ 4.40 (t, J = 6 Hz, 4 H) and 6.60 (d, J = 6 Hz, 8 H), attributable to the cumulene and methylene protons, respectively. The ir spectrum (KBr) had a band at 1701 cm^{-1} (C=O), but no appreciable absorption in the cumulene region (2000 cm^{-1}) and the electronic spectrum [λ_{max}^{EtOH} 223 nm (ϵ 15,000), 244 (26,000), 290 sh (4250), Figure 1] was consistent with the assigned structure.

The dione **6** is considerably more stable than the diketal **5** and could be stored at room temperature either in solution or the crystalline state. In the preparation of **5** from the tetrabromide precursors, no evidence for any other product was obtained. The simplicity of the nmr spectra of **5** and **6** suggests that in these compounds both of the cumulene groups have the same stereochemistry. Reasonably strain-free models of both the cis,cis and the trans,trans cumulenes can be made (see Figure 2), and the actual stereochemistry of these compounds is unknown. The temperature dependence of the nmr spectrum of **5** shows that it has a flexible conformation, but insufficient data are presently available to establish the barriers operating in this process.

The further ring expansion of the diketal **5** to **8** was examined. Reaction of a solution of **5** in pentane with excess bromoform and potassium *tert*-butoxide at −10° gave the bis(dibromocarbene) adduct **7**,

(5) A. T. Blomquist and R. D. Spencer, *J. Amer. Chem. Soc.*, **70**, 30 (1948); F. Sondheimer and Y. Gaoni, *ibid.*, **81**, 6301 (1959).

(6) These are minimal absorption values based on complete conversion of the bis(dibromocarbene) adducts.

(7) For example, see W. J. Ball, S. R. Landor, and N. Punja, *J. Chem. Soc. C*, 194 (1967).

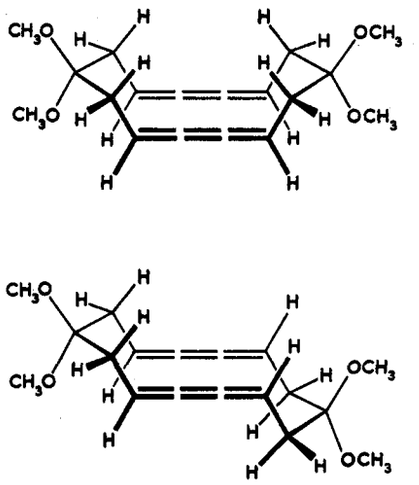
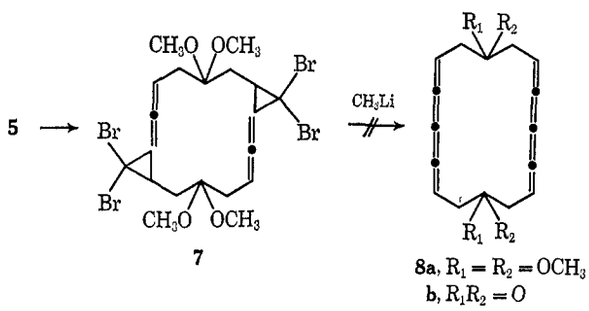


Figure 2.—The alternative cis,cis (above) and trans,trans (below) configurations of **5**.

mp ~140° dec. The gross structure of **7** follows from the analytical and mass spectral data. The nmr spectrum showed a 1:1 ratio of the olefinic to cyclopropyl hydrogens, indicating that addition had occurred to the terminal and not to the central double bonds of **5**. The spectrum also showed only a single methoxyl resonance, and these data are best accommodated by the symmetric structure **7**. The poor yield of **7**, together



7

8a, $R_1 = R_2 = OCH_3$
b, $R_1R_2 = O$

with its low stability at room temperature, precluded an extensive study of its reaction with methyllithium. However, this reaction was found to give a very unstable product, for which no structural evidence could be adduced.

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Ir spectra were recorded on either a Unicam SP 200 or a Perkin-Elmer 247 spectrophotometer, and only strong and medium bands are reported. Nmr spectra were recorded on a Varian HA-100 spectrometer as solutions in $CDCl_3$, unless stated otherwise, with TMS as internal standard and are reported in τ units. Mass spectra were recorded on either an AEI MS9 or MS12 spectrometer and were taken at 70 eV.

Silica for preparative thick layer chromatography (ptlc) was Merck Kieselgel GF_{254}, and that for column chromatography was Hopkins and Williams silica gel (MFC). Bromoform was dried ($CaCl_2$) and freshly distilled over P_2O_5 under N_2. Methyllithium in ether was obtained commerically from Alfa Inorganics. Solvents were May and Baker "R" grade and were purified and dried by standard methods.

Reaction of a Mixture of Racemic (1) and *meso*-5,5,11,11-Tetramethoxy-1,2,7,8-cyclodecatetraene (3) with Excess Bromoform and Potassium *tert*-Butoxide.—The diallenes **1** and **3** (350 mg, 1.25 mmol) and bromoform (3.20 g, 12.6 mmol) were dissolved in dry pentane (20 ml). The solution was cooled to 0° under N_2 and stirred and potassium *tert*-butoxide (sublimed, 1.40

g, 12.5 mmol) was added in portions over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 2 hr. Ether (100 ml) was added, the mixture filtered, and the residue washed with ether (100 ml). The combined ethereal layers were dried; the solvent was removed by evaporation and the residue chromatographed by ptlc on silica, eluting with pentane–ether (85:15). The four adducts in order of decreasing R_f value were as follows.

(i) Isomer **2b**: 50 mg (6.5%; mp 95–97° dec; mass spectrum *m/e* 596, 594, 592 (1), 590, 588 (1:4:6:4:1, $M^+ - CH_4O$), 565, 563, 561 (3), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (2.5), 541 (1:3:3:1, $M^+ - Br$), 515, 513, 511 (1.5), 509 (1:3:3:1, $M^+ - CH_4OBr$), 483, 481, 479 (3), 477 (1:3:3:1, $M^+ - C_2H_8O_2Br$), 401, 399 (3), 397 (1:2:1, $M^+ - C_2H_9O_2Br_2$), 95 (100); ir (KBr) 2960, 2840, 1750, 1454, 1439, 1300, 1282, 1256, 1233, 1222, 1194, 1135, 1121, 1055, 1044, 921, 748, and 719 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84. Found: C, 34.95; H, 4.10.

(ii) Isomer **4b**: 80 mg (10.5%); mp 77–78°; mass spectrum *m/e* 596, 594, 592 (0.3), 590, 588 (1:4:6:4:1, $M^+ - CH_4O$), 565, 563, 561 (1.5), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (1), 541 (1:3:3:1, $M^+ - Br$), 515, 513, 511 (1), 509 (1:3:3:1, $M^+ - CH_4OBr$), 95 (100); ir (KBr) 2940, 1740, 1452, 1440, 1362, 1304, 1289, 1234, 1190, 1137, 1128, 1103, 1073, 1060, 1054, 1038, 1035, 1020, 914, 892, 859, 780, 725, 718, and 708 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84. Found: C, 34.76; H, 3.94.

(iii) Isomer **2a**: 130 mg (16.5%); mp 117–118° dec; mass spectrum *m/e* 596, 594, 592 (0.1), 590, 588 (1:4:6:4:1, $M^+ - CH_4O$) 565, 563, 561 (0.4), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (0.4), 541 (1:3:3:1, $M^+ - Br$), 483, 481, 479 (0.7), 477 (1:3:3:1, $M^+ - C_2H_8O_2Br$), 469, 467, 465 (0.8), 463 (1:3:3:1, $M^+ - C_3H_{10}O_2Br$), 95 (100); ir (KBr), 2960, 1305, 1280, 1228, 1193, 1126, 1101, 1065, 1050, 987, 750, 715, and 695 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84; Br, 51.28. Found: C, 34.44; H, 3.89; Br, 51.26.

(iv) Isomers **3a**: 250 mg (32%); mp 79–80° dec; mass spectrum *m/e* 565, 563, 561 (0.2), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (0.3), 541 (1:3:3:1, $M^+ - Br$), 483, 481, 479 (0.01), 477 (1:3:3:1, $M^+ - C_2H_7O_2Br$), 95 (100); ir (KBr) 2955, 1745, 1438, 1303, 1275, 1224, 1194, 1128, 1073, 1055, 1040, 985, 935, 775, 719, and 708 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84; Br, 51.28. Found: C, 34.43; H, 4.00; Br, 50.78.

Reactions of the pure racemic diallene **1** (56 mg, 0.2 mmol) under the same conditions gave a mixture of the isomers **2a** (56.6 mg, 45%) and **2b** (22.5 mg, 18%), whereas reaction of the pure *meso*-diallene **3** (56 mg, 0.2 mol) gave a mixture of the isomer **4a** (62 mg, 50%) and **4b** (19 mg, 15%).

6,6,13,13-Tetramethoxycyclotetradeca-1,2,3,8,9,10-hexaene (5).—The mixture of bis(dibromocarbene) adducts **2a**, **2b**, **4a**, **4b** (100 mg, 0.15 mmol) was suspended in dry, degassed ether (5 ml) and the mixture cooled to −80° under N_2. Methyllithium (0.5 ml, 1 *M*, 0.5 mmol) was added to the magnetically stirred suspension, which was then allowed to warm to −10° and stirred for a further 30 min. Water (1 ml, distilled, degassed) was added, and the ether layer was rapidly separated and washed with water (0.5 ml, distilled, degassed). The solution was dried ($MgSO_4$) at 0° and filtered through neutral alumina (2 × 5 cm column) into a dry, N_2-filled flask at −10°. The solvent was removed by a stream of N_2 below 0° to give 6,6,13,13-tetramethoxy-1,2,3,8,9,10-cyclotetradecahexaene (**5**): mass spectrum *m/e* 304 (M^+, 63), 273 ($M^+ - CH_3O$, 38), 257 ($M^+ - C_2H_7O$, 19), 241 ($M^+ - C_2H_7O_2$, 13), 182 (35), 125 (31), 111 (44), 109 (40), 105 (63), 97 (63), 85 (60), 83 (53), 57 (100); ir (CCl_4) 2940, 2830, 1470, 1455, 1440, 1344, 1335, 1250, 1120, 1060, 875, and 703 cm^{-1}; nmr, see discussion; electronic spectrum, see discussion and Figure 1.

Reaction of either **2a** or **4a** under the same conditions gave a product identical in all observed respects with **5**.

Hydrogenation of 5.—The dicumulene **5** (obtained from **2a**, 200 mg, 0.32 mmol) was dissolved in ethyl acetate (10 ml) at 0°, palladium on charcoal (100%; 15 mg) was added, and the mixture was stirred at 0° for 3.5 hr under a H_2 atmosphere. The catalyst was removed by filtration; the filtrate evaporated under reduced pressure to give a crystalline residue. Recrystallization from pentane gave 1,8-cyclotetradecanedione (55 mg, 76% based on **2a**), identical in all observed respects with an authentic sample.[5]

3,4,5,10,11,12-Cyclotetradecahexaene-1,8-dione (6).—The diketal **5** (obtained from **2a**, 200 mg, 0.32 mmol) was dissolved in ether (50 ml) and shaken with sulfuric acid (80%, 5 ml) at 0° for 1 min. The ether layer was separated, washed quickly with water (2 × 5 ml), and filtered through silica (2 × 5-cm column). Cooling the filtrate gave 3,4,5,10,11,12-cyclotetradecahexaene-1,8-dione (**6**): mp ~130° dec (51 mg, 75% yield based on **2a**); mass spectrum *m/e* M^+ 212.0827; calcd for $C_{14}H_{12}O_2$, 212.0837; 212 (M^+, 50), 184 ($M^+ - CO$, 52), 183 (34), 170 (16), 169 (23), 157 (19), 156 (79), 155 (99), 142 (41), 141 (100), 134 (65), 132 (60), 78 (47); ir (KBr) 1701, 1433, 1404, 1335, 1215, 1113, 930, and 714 cm^{-1}; nmr, see discussion; electronic spectrum, see discussion and Figure 1.

Reaction of 5 with Excess Bromoform and Potassium *tert*-Butoxide.—The dicumulene **5** (obtained from **2a**, 208 mg, 0.33 mmol) was dissolved in dry pentane (75 ml) and the solution cooled to −10° under N_2 with stirring. Bromoform (843 mg, 3.3 mmol) was added, and then potassium *tert*-butoxide (sublimed, 373 mg, 3.3 mmol) was slowly added over 30 min. The reaction mixture was then allowed to warm to 0° and was stirred for a further 1 hr. Ether (50 ml) was added, the mixture filtered, and the residue washed with ether (50 ml). The combined ethereal layers were evaporated, and trituration of the residue with methanol gave 8,8,16,16-tetrabromo-5,5,13,13-tetramethoxytricyclo[13.1.0.0^{7,9}]hexadeca-1,2,9,10-tetraene (**7**): mp 140° dec (22 mg, 10%); mass spectrum *m/e* 621, 619, 617, 615, 613 (1:4:6:4:1, $M^+ - CH_3O$), 589, 587, 585, 583, 581 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 508, 506, 504, 502 (1:3:3:1, $M^+ - C_2H_7O_2Br$), 427, 425, 423 (1:3:1, $M^+ - C_2H_7O_2Br_2$); ir (CCl_4) 2970, 2700, 1460, 1440, 1308, 1280, 1257, 1198, 1129, 1080, 1060, and 878 cm^{-1}; nmr (60 MHz, CCl_4) 3.73 (m, 2 H, allene), 672 (s, 12 H, OCH_3), 7.2–8.1 (m, 8 H, CH_2), 8.3–8.8 (m, 2 H, cyclopropyl); electronic spectrum (EtOH), 237 nm.

Reaction of **7** (32.5 mg, 0.05 mmol) with methyllithium (0.2 ml, 1 *M*, 0.2 mmol) gave an unstable product which rapidly polymerized.

Registry No.—**1**, 29900-90-1; **2**, 40169-06-0; **3**, 29900-91-2; **4**, 40169-08-2; **5**, 34059-86-4; **6**, 34059-87-5; **7**, 40169-11-7; bromoform, 75-25-2; potassium *tert*-butoxide, 865-47-4; methyllithium, 917-54-4.

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cis,trans-5,6,7,8-Diepoxy-8-carboxamido-5,6,7,8-tetrahydrotetrazolo[1,5-*a*]pyridine

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The pyridine ring opening of 8-nitro- and 8-cyanotetrazolo[1,5-*a*]pyridines (**1a** and **1b**) in sodium hydroxide solution was described recently.[1] As part of this study we required 8-carboxamidotetrazolo[1,5-*a*]-pyridine (**1c**). The preparation of this compound was attempted by treatment of the nitrile **1b** with an ethanolic solution of potassium hydroxide and hydrogen peroxide.[2] However, the highly crystalline product **2**, mp 240° dec, obtained in high yield, exhibited none of

(1) B. Stanovnik and M. Tislér, *Chimia*, **25**, 272 (1971).
(2) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961).