H, methylene), 4.38 (J = 264 Hz, t, 1 H, methine). This compound is considered to be **5**, the cis isomer. To 0.300 g of **2** dissolved in 50% aqueous ethanol was added sufficient aqueous sodium hydroxide to give a pH value of 10. Ethyl iodide (0.30 g) was added, the solution stirred until a negative value for sulfhydryl group was obtained (Folin's reagent), the solution acidified to pH 1, the ethanol removed by flash evaporation under reduced pressure, the residual aqueous solution extracted with ethyl ether, and the ethereal extract evaporated to leave 0.180 g of **3** which, after recrystallization from ethyl ether–Skellysolve B, melted at 115–117°: neutralization equivalent, 120.5 (calcd 118.2); nmr (CF_3COOH) δ 1.31 (J = 79 Hz, t, 3 H, methyl), 2.75 (J = 165 Hz, multiplet, 6 H, methylene), 4.47 (J = 257 Hz, t, 1 H, methine). *Anal.* Calcd: C, 40.66; H, 5.12; S, 27.14. Found: C, 41.11; H, 5.38; S, 26.64.

Treatment of 0.300 g of **5** with 0.30 g of ethyl iodide as above gave 0.245 g of **6** which, after recrystallization from chloroform–ethyl ether, melted at 156-158°: nmr (CF_3COOH) δ 1.31 (J = 79 Hz, t, 3 H, methyl), 2.75 (J = 165 Hz, multiplet, 6 H, methylene), 4.47 (J = 258 Hz t, 1 H, methine.) *Anal.* Calcd: C, 40.66; H, 5.12; S, 27.14. Found: C, 40.78; H, 5.14; S, 26.91.

Transformation of Racemic 1,2-Dithiane-3,6-dicarboxylic Acid (4) into 2-Mercaptothiolane-2,5-dicarboxylic Acid and of the Latter into Its *S*-Ethyl Derivative.—In a procedure that differed from the immediately preceding one only in that the concentration of sodium hydroxide was ~3 *N*, 3.30 g of **4** was transformed into 2.70 g of solid thiol which was fractionated into 0.80 g of **2** (30%) and 1.90 g of **5** (70%). From both **2** and **5** the *S*-ethyl derivatives, **3** and **6**, were prepared as before.

Transformation of Dithiodisuccinic Acid (9) into 2-Mercapto-3-thiapentane-1,2,4,5-tetracarboxylic Acid (10) and of 10 into *S*-Ethylmercaptosuccinic Acid (11).—**9** (1.12 g) was dissolved in a solution of 12.5 g of sodium hydroxide in 100 ml of water at room temperature under nitrogen. After ~2 hr the absorbance at 296 nm had reached a maximum. Ethyl iodide and sufficient ethanol to give a homogeneous solution were then added. When the test for the sulfhydryl group was negative, the solution was acidified to pH 2 and partially evaporated under reduced pressure, the residual aqueous solution extracted with ethyl ether, and the ethereal extract dried with magnesium sulfate and evaporated to dryness to give 1.17 g of a product which, after recrystallization from chloroform–Skellysolve B, melted at 95-97°. This product was identical in melting point and nmr spectrum with an authentic specimen of **11** prepared by alkylating mercaptosuccinate with ethyl iodide. Again, 3.14 g of **9** was dissolved in a solution of 6.0 g of sodium hydroxide in 100 ml of water under nitrogen. When the absorbance maximum at 296 nm was attained, the solution was neutralized to pH 10.0 and evaporated to dryness. After holding the residue over phosphorus pentoxide for some time, it was redissolved in water and the absorbance at 296 nm was found to be comparable to the previous value.

Acknowledgment.—We are grateful to the National Institutes of Health for the support afforded by Grant AM-13109.

Registry No.—**1**, 28463-60-7; **2**, 28463-61-8; **3**, 28463-62-9; **4**, 2611-41-8; **5**, 28463-64-1; **6**, 28463-65-2; **7**, 28463-66-3; **9**, 3384-95-0; **12**, 4695-07-2; *meso*-1,2-dithiane-3,6-dicarboxylic acid diethyl ester, 28463-67-4.

The Synthesis of 6,6'-Diethynyldiphenic Anhydride[1]

MELVIN S. NEWMAN* AND MARSHALL W. LOGUE[2]

McPherson Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210

Received September 26, 1970

The synthesis of 6,6'-diethynyldiphenic anhydride (**10**) is described (Scheme I). Methyl 2,3-diiodobenzoate (**2**) was heated with copper bronze to yield dimethyl 6,6'-diiododiphenate (**3**). Heating **3** with carbethoxyethynylcopper in pyridine yielded dimethyl 6,6'-bis(carbethoxyethynyl)diphenate (**6**) which, by preferential alkaline hydrolysis, was converted into dimethyl 6,6'-bis(carboxyethynyl)diphenate (**8**). After decarboxylation of **8**, the resulting ester was hydrolyzed to 6,6'-diethynyldiphenic acid (**9**). Treatment of **9** with ethoxyacetylene afforded **10** which is stable thermally up to about 200° when decomposition to yield dark polymeric material occurs. A few attempts at photolysis of **10** yielded unchanged **10** in almost quantitative yield. Heating of **2** with copper in dimethylformamide at 55° yielded 1,5-dicarbomethoxybiphenylene (**4**). In pyridine **3** yielded a small amount of 1,8-dicarbomethoxybiphenylene (**5**) on heating with copper. Intramolecular Ullmann coupling of 2-iodo-3-ethylbenzoic anhydride (**15**) proceeded in 90% yield on refluxing in DMF for 15 min, whereas conventional Ullmann coupling of methyl 2-iodo-3-ethylbenzoate (**14**) was much slower.

In this paper, the synthesis of 6,6'-diethynyldiphenic anhydride (**10**) is reported. This compound was synthesized because we wished to know whether or not the substituted tetrahedrane (**11**) would be formed on pyrolysis or photolysis. The most highly strained and condensed ring system containing carbon–carbon single bonds is that of tricyclo[1.1.0.0.^{2,4}]butane (tetrahedrane). The strain energy for tetrahedrane has been calculated to be 90 and 151 kcal/mol, respectively.[3,4]

Since attempted syntheses of tetrahedranetricarboxylic acid were reported,[5,6] a number of papers[7-11] dealing with unsuccessful attempts to prepare tetrahedranes have appeared. The synthesis of 6,6'-diethynyldiphenic anhydride (**10**) was undertaken because **10** seemed to offer the greatest chance to yield a tetrahedrane compound. Molecular models indicated that the two ethyl groups cross each other at about an 80° angle and the anhydride function supposedly would force the two ethynyl groups as close to each other as nonbonded interaction would allow. Furthermore, nmr analysis would readily show the loss of the acetylenic hydrogens in any product.

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(1) This work was supported in part by Grant 5552 of the National Science Foundation.

(2) Holder of the Sinclair Oil Fellowship, The Ohio State University, 1966–1967. Further details may be found in the Ph.D. Thesis of M. W. L., The Ohio State University, 1969.

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Theoretical considerations[12] predict that the transformation of two acetylenes to tetrahedrane would be a chemically allowed process. Two crossed acetylenes, 2,2′-bis(phenylethynyl)biphenyl (**12**)[8] and 2,2′-diethynylbiphenyl (**13**),[10] have been studied previously; however, the acetylenic groups in **12** and **13** are not forced together in a crossed position as they are in **10**. Whereas **12** gave 9-phenyldibenz[*a,c*]anthracene both photochemically and thermally, photolysis of **13** resulted in an almost quantitative recovery of starting material.

A modified isatin synthesis[13] was used for the preparation of 3-iodoanthranilic acid (**1**) from *o*-iodoaniline. Treatment of methyl 2,3-diiodobenzoate (**2**) with copper bronze at 110° afforded dimethyl 6,6′-diiododiphenate (**3**) in 61% yield. Ullmann reactions on 2,3-dihalogenated aromatic compounds which contain nitro and carbomethoxy activating groups yield only products derived from coupling at the ortho position.[14] The structure of **3** was established by conversion to **5** (see Experimental Section).

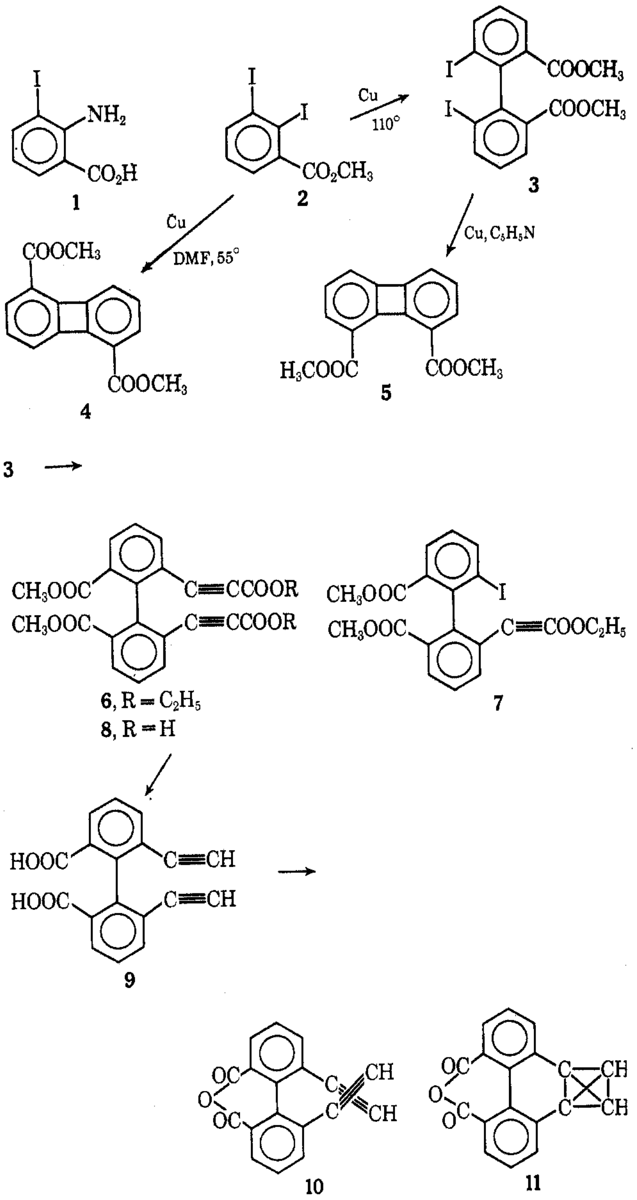
Interestingly, when **2** was heated with copper bronze in DMF at 55°, 1,5-dicarbomethoxybiphenylene (**4**) was produced in 75% yield.[15,16] On heating **3** with copper in pyridine, the isomeric 1,8-dicarbomethoxybiphenylene (**5**) was formed in 11% yield (Scheme I).

Dimethyl 6.6′-bis(carbethoxyethynyl)diphenate (**6**) was synthesized from **3** and carbethoxyethynylcopper (2 equiv) in pyridine at reflux.[17] Despite numerous attempts, yields of only 4–5% of **6** (about 50% recovery of **3**) were obtained. Some dimethyl 6-iodo-6′-carbethoxyethynyldiphenate (**7**) and biphenylene (**5**) were also produced. **7** was converted into **6** in 18% yield by treatment with additional carbethoxyethynylcopper.

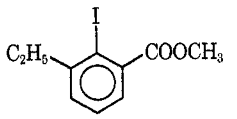
Selective saponification of **6** with sodium hydroxide (2 equiv) afforded dimethyl 6,6′-bis(carboxyethynyl)-diphenate (**8**) which was smoothly converted into 6,6′-diethynyldiphenic acid (**9**) by decarboxylation[18a] followed by alkaline hydrolysis. By treatment with ethoxyacetylene[18b] **9** was cyclized to the anhydride (**10**). Correct analysis for C and H of **10** was unsuccessful owing to its great tendency to react with water to form **9**. This tendency was also annoying in attempts to run photolyses on dilute solutions and to take nmr spectra. However, sharp melting points for **10** could be obtained in sealed tubes and the practically quantitative conversions of **10** to **9** indicated that **10** was pure. A precise mass spectral analysis on **10** gave the expected values.

Photolyses of **10** in methylene chloride were performed in Pyrex and quartz nmr tubes, with and without benzophenone as a sensitizer. After each run the nmr and ir spectra were identical with those obtained before irradiation, and unchanged **10** was recovered. Pyrolyses of **10** in *sym*-tetrachloroethane in sealed tubes at temperatures of 180° and below showed that no reaction had occurred. At 200° dark solutions were obtained which gave no acetylenic hydrogen bands at 6.80, but only polymeric material was present.

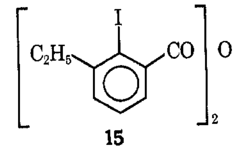
SCHEME I



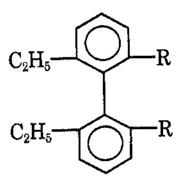
During work on an alternate (but unsuccessful) synthesis of **10**, the Ullmann coupling of methyl 2-iodo-3-ethylbenzoate (**14** to **16b**) was effected in 41% yield by heating with copper bronze in refluxing DMF for 15



14



15



16a, R = CO_2H
b, R = CO_2Me

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(12) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

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(15) See ref 14a and 14b.

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min. However, when **14** was hydrolyzed to the corresponding acid and the latter converted into the anhydride (**15**), similar Ullmann treatment yielded (after hydrolysis) **16a** in 90% yield. Judging from this example, if Ullmann couplings are converted into intramolecular couplings as above, improved yields may result.[19]

Experimental Section[20]

2-Iodoaniline (17).—The preparation of **17**, mp 58.0–58.5°, from *o*-nitroaniline was effected essentially as described[21] in 90% yield.

2-Iodo-α-isonitrosoacetanilide (18).—To a well-stirred solution of 371 g (2.25 mol) of chloral hydrate, 345 g (5.0 mol) of hydroxylamine hydrochloride, and 1.42 kg (10.0 mol) of anhydrous Na_2SO_4 in 7 l. of water was added a mixture of 160 g of concentrated HCl, 328 g (1.5 mol) of **17**, and 1 l. of water. The resulting mixture was slowly heated to 37° during 2.5 hr, at which time a yellow solid began to appear. The temperature of the reaction mixture was then slowly raised to 45° (2 hr). After cooling to room temperature, the product was filtered to yield 355 g (82%) of **18**, mp 158–160°. Recrystallization from ethanol gave colorless crystals, mp 167–168° (lit.[22] mp 162°).

7-Iodoisatin (19).—To 550 ml of 86% (by weight) H_2SO_4 at 55° was added 140 g (0.49 mol) of **18** during 25 min with efficient stirring. After the final portion of **18** had been added, the reaction mixture was allowed to warm to 70° and then stirred for an additional 20 min. The purplish-red mixture was then poured over crushed ice and the resulting precipitate collected. The filter cake was dissolved in 10% aqueous KOH and filtered through Celite. The filtrate was carefully acidified with 10% HCl until a precipitate just began to form, and then an additional 20 ml was added. After filtration through Celite, the filtrate was acidified with concentrated HCl to give 101 g (80%) of **19**. A sample was recrystallized from methanol to give bright red crystals, mp 221–222° (lit.[22] mp 209°).

3-Iodoanthranilic Acid (1).—To a well-stirred solution of 164 g (0.6 mol) of **19** and 40.4 g (0.7 mol) of KOH in 350 ml of H_2O at 0° was added a chilled solution of 117 g (1.0 mol) of 30% H_2O_2 and 57.6 g (2.1 mol) of KOH in 800 ml of H_2O during 1.25 hr with the temperature kept below 10° throughout the addition. After an additional 45 min of stirring, 220 ml of glacial acetic acid was added during 30 min with an occasional addition of a few drops of 2-octanol to reduce extreme foaming. Filtration afforded 154 g (95%) of **1**. A sample was recrystallized (aqueous-acetone) to give light yellow needles, mp 182–183° (lit.[22] mp 176–177°).

Methyl 2,3-Diiodobenzoate (2).—To a well-stirred mixture of 29 g (110 mmol) of **1**, 32 g (330 mmol) of concentrated HCl, and 100 ml of water at 0° was added a chilled solution of 9.4 g (110 mmol) of KNO_2 in 100 ml of water during 10 min. After a stirring period of 1 hr at 0°, a chilled solution of 39.8 g (240 mmol) of KI in 100 ml of water was added. The reaction mixture was allowed to warm to room temperature and decolorized with excess $NaHSO_3$. The light tan precipitate was filtered to afford 34.5 g (82%) of 2,3-diiodobenzoic acid. A sample was recrystallized from ethanol to give colorless crystals, mp 183–185° (lit.[23] mp 178–181°). Treatment with diazomethane yielded **2**, the nmr spectrum of which showed three aromatic hydrogens in the τ 2–3 region and a CH_3 peak at τ 5.5 (3 H).

Anal. Calcd for $C_8H_6I_2O_2$: C, 24.8; H, 1.6. Found: C, 25.2; H, 1.6.

Dimethyl 6,6′-Diiododiphenate (3).—To 50 g (129 mmol) of **2** at 110° was added 24.6 g of activated[24] copper bronze during 1 hr with stirring. After 1 hr at 110°, another 24.6 g of activated copper bronze was added in one portion. The mixture was held at 110–115° for 3 hr, cooled, and extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the residue washed with cold ether to afford 20.3 g (61%) of **3**. The ether was removed from the washings to give 15.1 g (31%) of recovered **2**. Recrystallization of the ether residue from ethanol gave colorless crystals of **3**: mp 147–148°; ir (KBr) bands at 5.72 and 5.80 μ; nmr ($CDCl_3$) at τ 6.38 (s, 6, OCH_3), 2.92 (t, 2, J = 8 Hz, 4- and 4′-Ar H), 2.05 (q, 2, J = 1.8 Hz, 5- and 5′-Ar H), 1.95 (q, 2, J = 1.8 Hz, 3- and 3′-Ar H).

Anal. Calcd for $C_{16}H_{12}I_2O_4$: C, 36.8; H, 2.3; I, 48.6. Found: C, 36.9; H, 2.4; I, 48.8.

1,8-Dicarbomethoxybiphenylene (5).—To a solution of 520 mg (1.0 mmol) of **3** in 20 ml of dry pyridine was added 130 mg of activated copper bronze.[24] After having been stirred at reflux for 20 hr, the reation mixture was cooled and worked up as usual with ether to give a brown oil. Column chromatography of the oil on silica (10% ether–benzene) afforded 440 mg (87%) of recovered **3** and 30 mg (11%) of **5**. Recrystallization from ethanol gave bright yellow needles: mp 147–148°; ir ($CHCl_3$) 5.85 μ; uv (ethanol) λ_{max} 250 mμ (ε 30,700), 350 (sh, 3410), 365 (5270); nmr ($CDCl_3$) τ 6.17 (s, 6, OCH_3), 3.17 (m, 6, Ar H).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5. Found: C, 71.8; H, 4.6.

1,5-Dicarbomethoxybiphenylene (4).—To a stirred solution of 1.9 g (5 mmol) of **2** in 15 ml of dry DMF at 55° was added 1.9 g of activated copper bronze. After stirring for 2 hr at 55°, the reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was worked up as usual to afford a yellow semisolid. The semisolid was collected and washed with cold acetone to give 500 mg (75%) of **4**. From the filtrate 270 mg (14%) of **2** was recovered. Recrystallization (acetone) of **4** gave light yellow needles: mp 187–188°; ir ($CHCl_3$) 5.85 μ; uv (ethanol) λ_{max} 254 mμ (ε 38,900), 263 (42,300), 372 (8850), 393 (11,400); nmr ($CDCl_3$), τ 6.17 (s, 6, OCH_3), 3.05 (m, 4, Ar H), 2.88 (dd, 2, J = 7.5 and 3 Hz, Ar H).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5. Found: C, 71.5; H, 4.5.

A sample of **3** was saponified to yield the diacid, mp >360° dec. This diacid was stirred for 15 hr with ethoxyacetylene in methylene chloride. The resulting anhydride, mp 240° dec, ir (CH_2Cl_2) 5.6 and 5.7 μ, was obtained in high yield.

Anal.. Calcd for $C_{14}H_8I_2O_4$: C, 34.0; H, 1.6. Found: C, 34.3; H, 1.7. Calcd for $C_{14}H_6I_2O_3$: C, 35.2; H, 1.3. Found: C, 35.5; H, 1.3.

Mass spectra of **4** and **5** gave parent peaks at M^+ 268. A strong peak at M^+ 237 in **5** (much weaker in **4**) provides additional evidence for the 1,8 location of the carbomethoxy groups as the acylium ion formed by loss of CH_3O is stabilized by the adjacent carbomethoxy group.[25]

Carbethoxyethynylcopper.—To a well-stirred mixture of 19 g (50 mmol) of cuprous iodide,[26] 31.2 g (400 mmol) of $(NH_4)_2CO_3$, and 400 ml of distilled water under nitrogen was added a solution of 9.8 g (100 mmol) of ethyl propiolate in 150 ml of ethanol. After having been stirred for 30 min under nitrogen, the reaction mixture was filtered and the filter cake was washed successively with 200 ml each of water, ethanol, and ether. The filter cake was air-dried to give 16.1 g (100%) of canary yellow carbethoxyethynylcopper: ir (mineral oil) 5.2, 5.86, and 5.95 μ.

Dimethyl 6,6′-Bis(carbethoxyethynyl)diphenate (6).—In the best of many experiments 60 ml of pure degassed dry pyridine was added to a mixture of 10.0 mmol of **3** and 22.0 mmol of carbethoxyethynylcopper which had been stirred under dry N_2 for 15 min. After 24 hr at 110°, the mixture was cooled, diluted with CH_2Cl_2, filtered through Celite, and worked up as usual. By column chromatography on silica gel (2 and 4% ether–benzene for **7** and **6**, respectively) and crystallization from ethanol there was isolated about 16% of **7** [mp 105–107°; ir (KBr) bands at 4.48, 5.8, and 5.9 μ] and 5% of **6** (mp 87.5–89.5°; ir bands as for **7**): nmr ($CDCl_3$) for **6**, τ 8.83 (t, 6, J = 7.5 Hz, OCH_2CH_3),

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[19] We thank Dr. John S. Swenton for valuable advice concerning the photochemical experiments.

[20] All melting points and boiling points are uncorrected. All microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Ir spectra were obtained with Perkin-Elmer 237 and/or 137 instruments. Uv spectra were obtained on a Bausch and Lomb Spectronic 505 or a Cary Model 15 spectrophotometer. Nmr spectra were obtained with a Varian A-60 spectrometer in reference to tetramethylsilane as an internal standard. All column chromatography was performed on Grace Davison 950 silica gel. The term "worked up as usual" means that a solution of the products in an organic solvent after washing with dilute alkali and/or acid, water, and saturated salt solution was filtered through 10–20 mesh Drierite (anhydrous calcium sulfate). The solvent was then removed on a rotary evaporator.

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[24] Commercial copper bronze (Venus 44-F natural copper, U. S. Bronze Powders, Inc., Flemington, N. J.) was activated as described by E. C. Kleiderer and R. Adams, *J. Amer. Chem. Soc.*, **55**, 4219 (1933).

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[26] G. B. Kauffman and R. P. Pinnell, *Inorg. Syn.*, **6**, 3 (1960).

6.38 (s, 6, OCH_3), 5.91 (q, 4, J = 7.5 Hz, OCH_2CH_3), 2.55 (t, J = 8 Hz, 4- and 4'-Ar H), 2.16 (dd, 2, J = 8 and 1.5 Hz, 5- and 5'-Ar H), 1.84 (dd, 2, J = 8 and 1.5 Hz, 3- and 3'-Ar H); for **7**, 8.82 (t, 3, J = 7.5 Hz, OCH_2CH_3), 6.37 (s, 3, OCH_3), 6.33 (s, 3, OCH_3), 5.90 (q, 2, J = 7.5 Hz, OCH_2CH_3), 2.20 (complex m, 6, Ar H).

Anal. Calcd for $C_{16}H_{22}O_8$ (**6**): C, 67.5; H, 4.8. Found: C, 67.7; H, 4.8. Calcd for $C_{21}H_{17}IO_6$ (**7**): C, 51.2; H, 3.5. Found C, 51.4; H, 3.4.

Dimethyl 6,6'-Bis(carboxyethynyl)diphenate (8).—Alkaline hydrolysis of **6** for 1 hr in boiling aqueous methanol containing 2 equiv of NaOH yielded **8** quantitatively. Recrystallization from chloroform gave colorless **8**: mp 158–162° dec; nmr (acetone-d_6) τ 6.39 (s, 6, OCH_3), 2.48 (t, 2, J = 8 Hz, 4- and 4'-Ar H), 2.15 (dd, 2, J = 8 and 1.5 Hz, 5- and 5'-Ar H), 1.81 (dd, 2, J = 8 and 1.5 Hz, 3- and 3'-Ar H).

Anal. Calcd for $C_{22}H_{14}O_8$: C, 65.0; H, 3.5. Found: C, 64.9; 3.5.

6,6'-Diethynyldiphenic Acid (9).—To 834 mg (2.1 mmol) of **8** was added 10 ml of *N,N*-dimethylaniline. After having been stirred for 1.75 hr at 110–120°, the reaction mixture was cooled, poured into excess 10% HCl, and worked up as usual with ether to give a brown residue. Chromatography on silica (benzene) afforded 606 mg of colorless material. To 110 mg of the above material was added 10 ml of 5% methanolic NaOH. After the mixture was refluxed for 20 hr, it was cooled, poured into excess 10% HCl, and worked up as usual with ether to give 100 mg (92% based on **8**) of **9**. Recrystallization from ethyl acetate gave colorless crystals of **9**: mp 251–254°; ir bands at 3.03 and 5.9 μ; nmr (DMSO-d_6) τ 6.17 (s, 2, $\equiv$CH), 2.54 (t, 2, J = 8 Hz, 4- and 4'-Ar H), 2.24 (dd, 2, J = 8 and 1.5 Hz, 5- and 5'-Ar H), 1.96 (dd, 2, J = 8 and 1.5 Hz, 3- and 3'-Ar H).

Anal. Calcd for $C_{18}H_{10}O_4$: C, 74.5; H, 3.5. Found: C, 74.7; H, 3.6.

6,6'-Diethynyldiphenic Anhydride (10).—To a stirred suspension of 20.2 mg (0.07 mmol) of **9** in dry CH_2Cl_2 was added 0.75 ml of 0.1 *M* ethoxyacetylene in CH_2Cl_2. After a stirring period of 24 hr, the solvent was removed under reduced pressure to afford 18.8 mg (100%) of **10**: mp 155° dec; ir ($CHCl_3$) bands at 3.03, 5.6, and 5.7 μ; nmr (CH_2Cl_2) at τ 6.80 (s, 2, $\equiv$CH), 2.25 (m, 6, aromatic); uv (ether) λ 232 mμ (ϵ 29,500), 253 sh (10,000) 300 (2050); mass spectrum (70 eV) *m/e* (rel intensity) 274 (2.5), 273 (20), 272 (100), 229 (10), 228 (52), 201 (16), 200 (92), 199 (27), 174 (19), 150 (13), 100 (31); mol wt (calcd for $C_{18}H_8O_3$) 272.047339, found 272.047418 (by mass spectrographic analysis).

On hydrolysis **10** was converted into **9**.

Photolyses of 6,6'-Diethynyldiphenic Anhydride (10).—A number of attempts to effect photochemical reactions were carried out at 0° in Pyrex and quartz nmr tubes strapped to a quartz immersion-well of a 450-W Hanovia medium-pressure lamp. All photolyses were conducted in CH_2Cl_2 and were 1.4×10^{-1} *M* in **10**. The sensitized photolyses were 1.1 *M* in benzophenone. The direct photolyses were conducted in Pyrex for periods of 0.5, 1.5, and 10.5 hr and in quartz for periods of 0.5 and 2.0 hr. The sensitized (Pyrex) photolyses were conducted for periods of 0.5 and 9.5 hr. In each case **10** was recovered essentially quantitatively.

Pyrolyses of 6,6'-Diethynyldiphenic Anhydride (10).—The pyrolyses of **10** were performed at 140, 160, 180, and 200° in sealed nmr tubes in 1,1,2,2-tetrachloroethane for 1 hr. Unchanged **10** was recovered in high yield in all but the 200° run. Pyrolyses at 200° were also performed for 15 and 30 min. Tarry material resulted.

2-Ethyl-α-isonitrosoacetanilide (20).—The procedure used for the preparation of **18** was used to prepare **20** in 86% yield from *o*-ethylaniline.[27] Recrystallization from water of **20** gave colorless needles, mp 105–106°.

Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.5; H, 6.3. Found: C, 62.4; H, 6.4.

7-Ethylisatin (21) was prepared in 81% yield as for **19**. Recrystallization (MeOH) of **21** gave rust colored crystals, mp 189–190° (lit.[28] mp 193°).

3-Ethylanthranilic acid (22) was prepared in 96% yield as for **1**. Recrystallization from acetic acid gave light tan needles, mp 147–148° (lit.[29] mp 146–147°).

Methyl 2-Iodo-3-ethylbenzoate (14).—To 832 g of concentrated HCl that was cooled in a Dry Ice–acetone bath was added a solution of 394 g (2.4 mol) of **22**, 118 g (2.9 mol) of NaOH, and 181 g (2.6 mol) of $NaNO_2$ in 2 l. of water at 10° during 1 hr with stirring. After 15 min, 20 g of urea was added followed by 830 g (5 mol) of KI during 15 min. After stirring for 1 hr, the dark mixture was decolorized with excess $NaHSO_3$ and the resulting light yellow precipitate collected to give crude 2-iodo-3-ethylbenzoic acid. To a solution of the crude acid in 2 l. of MeOH were added 250 g of 2,2-dimethoxypropane and 25 g of concentrated H_2SO_4. After 40 hr at reflux, 68 g of pyridine was added and the reaction mixture was concentrated under reduced pressure. After work-up with ether as usual, the residue was distilled to give 399 g (58%) of **14**, bp 114–116° (0.35 mm). A sample of **14** was saponified with 5% ethanolic KOH to give pure 2-iodo-3-ethylbenzoic acid, mp 110–112°, on crystallization from CCl_4.

Anal. Calcd for $C_9H_9IO_2$: C, 39.1; H, 3.3. Found: C, 38.9; H, 3.1.

2-Iodo-3-ethylbenzoic Anhydride (15).—To a solution of 6.8 g (23.5 mmol) of 2-iodo-3-ethylbenzoic acid in 25 ml of dry CH_2Cl_2 that was cooled in an ice bath was added 0.8 g (11.8 mmol) of ethoxyacetylene in 15 ml of CH_2Cl_2. After 24 hr, 6.3 g (100%) of **15** was obtained. Low-temperature recrystallization from ethyl acetate–hexane yielded colorless crystals of **15**: mp 50.0–50.5°; ir (neat) 5.55, 5.75 μ.

Anal. Calcd for $C_{18}H_{16}I_2O_3$: C, 40.4; H, 3.0; I, 47.6. Found: C, 40.3; H, 3.1; I, 47.3.

Ullmann Reaction on 2-Iodo-3-ethylbenzoic Anhydride (15).—To a refluxing solution of 3.8 g (7.1 mmol) of **15** in 100 ml of dry DMF was added 2.7 g of activated copper bronze. After having been stirred for 15 min, the reaction mixture was cooled, diluted with ether, filtered, and worked up as usual. The product was hydrolyzed with alkali. On acidification 1.9 g (90%) of 6,6'-diethyldiphenic acid (**16a**) was obtained. Recrystallization from ethyl acetate gave colorless crystals, mp 226–229°.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1. Found: C, 72.5; H, 6.1.

Ullmann Coupling of Methyl 2-Iodo-3-ethylbenzoate (14).—To a refluxing solution of 1.50 g (5.3 mmol) of **14** in 50 ml of dry DMF was added 1.50 g of activated copper bronze. The reaction mixture was stirred for 15 min, cooled, diluted with ether, and filtered. The filtrate was worked up in the usual manner to give a yellow oil. Column chromatography on silica afforded 700 mg (46%) of recovered **14** (benzene) and 360 mg (41%) of dimethyl 6,6'-diethyldiphenate (**16b**) (1% ether in benzene) which was saponified to **16a** for identification.

Registry No.—**2**, 14192-14-4; **3**, 28444-05-5; **3** diacid, 28444-06-6; **3** anhydride, 28444-07-7; **4**, 20275-25-6; **5**, 20275-26-7; **6**, 28444-10-2; **7**, 28455-59-6; **8**, 28455-60-9; **9**, 28455-61-0; **10**, 27287-05-4; **14**, 28455-63-2; **15**, 28455-64-3; **16a**, 7509-70-8; **20**, 7509-61-7.

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[27] We thank the Ethyl Corp. for a generous gift of *o*-ethylaniline.

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