methiodide (5.67 g) was added as the powder to a warm solution of 6.8 g of potassium *t*-butoxide (courtesy of the MSA Research Laboratories, Callery, Pa.) in 20 ml of *t*-butyl alcohol, whereupon the odor of trimethylamine was immediately detected. The yellow reaction mixture was heated under reflux for 4 hr, cooled, and diluted with water. The resulting slurry was separated by filtration and the precipitate was washed with ether and discarded. The aqueous phase was drawn off and extracted twice with ether. After removing the volatile solvents from the combined ether extracts by distillation at atmospheric pressure, the product was distilled under reduced pressure yielding 1.75 g (74%) of a colorless liquid with a characteristic odor remotely resembling that of wintergreen: bp 38° (0.3 mm) [lit.[3] bp 87.0–87.5° (15 mm)]; $n^{25}\text{D}$ 1.5183; $[\alpha]^{24}\text{D}$ +58.0° (*c* 0.242), $[\alpha]^{24}\text{D}$ +77.4° (*c* 1.69), $[\alpha]^{24}\text{D}$ +81.8° (*c* 4.22) [lit.[21] $n^{20}\text{D}$ 1.5198, $[\alpha]^{20}\text{D}$ +70.7° (*c* 4.39)]; $\lambda_{max}$ 217 mμ (log ε 4.06), 245 sh (2.00), 250 sh (2.15), 256 (2.27), 261 (2.35), 267 sh (2.24), and 270 sh (2.05). The nmr data are reported in Table II.

When a sample of the reaction product was subjected to gas chromatographic analysis under the same conditions as those described for the *cis*-oxirane, two peaks were obtained having a ratio of areas of 37:63. On addition of benzyl methyl ketone to the reaction product, only the relative areas of the two peaks was altered changing to 14:86.

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# Aziridines. XIII. Reactions of 1,2,3-Triarylaziridines with Activated Alkenes and Alkynes

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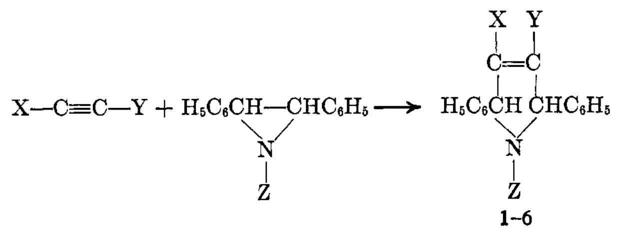
1,2,3-Triphenylaziridine and 1-*p*-bromophenyl-2,3-diphenylaziridine react with ethynes and ethenes in refluxing toluene or xylene to form 3-pyrrolines and pyrrolidines, respectively. A novel decarboxylative elimination of 3,4,5-triphenyl-1,2-dicarbethoxy-1,2,4-triazolidine into benzalazine and aniline is described.

A recent communication described the reaction of 1,2,3-triphenylaziridine with diethylacetylene dicarboxylate and maleic anhydride.[1] Carbon–carbon bond scission of the aziridine ring occurred in these reactions and the products were 1,2,5-triphenyl-3,4-dicarbethoxy-3-pyrroline and 1,2,5-triphenylpyrrolidine-3,4-dicarboxylic anhydride, respectively. Other aziridines were subsequently reported to form adducts with various ethenes and ethynes by carbon–carbon cleavage of the aziridine ring.[2,3]

We now wish to report in detail the reaction of 1,2,3-triphenylaziridine and 1-*p*-bromophenyl-2,3-diphenylaziridine with a number of alkynes and alkenes. In each instance carbon–carbon cleavage of the aziridine ring was observed.

Near-quantitative yields of 3-pyrrolines (1–6) were obtained when toluene or *p*-xylene solutions of 1,2,3-triphenylaziridine or 1-*p*-bromophenyl-2,3-diphenylaziridine were heated for several hours with diethylacetylene dicarboxylate, ethyl propiolate, dibenzoylacetylene, and hexafluoro-2-butyne.



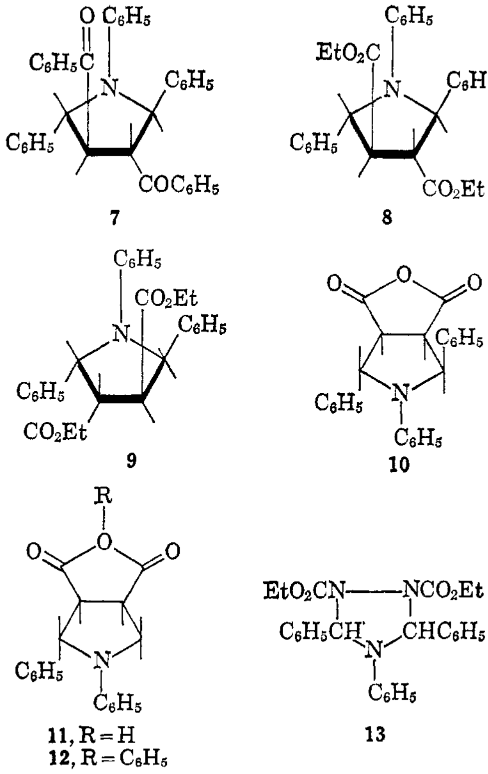
$$X\text{—}C{\equiv}C\text{—}Y + \underset{\underset{Z}{|}}{\underset{N}{H_5C_6CH\text{—}CHC_6H_5}} \longrightarrow \underset{\underset{Z}{|}}{\underset{N}{H_5C_6\overset{\overset{X\quad Y}{C=C}}{CH\;\;CH}C_6H_5}}$$

1–6

1, X, Y = $CO_2C_2H_5$; Z = $C_6H_5$
2, X = $CO_2C_2H_5$; Y = H; Z = $C_6H_5$
3, X, Y = $C_6H_5CO$; Z = $C_6H_5$
4, X, Y = $CF_3$; Z = $C_6H_5$
5, X, Y = $CO_2C_2H_5$; Z = *p*-$BrC_6H_4$
6, X, Y = $C_6H_5CO$; Z = *p*-$BrC_6H_4$

Heating toluene solutions of 1,2,3-triphenylaziridine with *trans*-dibenzoylethene, ethyl fumarate, ethyl maleate, maleic anhydride, maleimide, N-phenylmaleimide, and diethyl azodicarboxylate gave the adducts **7–13**, (Chart I), respectively. It is to be noted that the carbethoxy groups of the adduct **9** are *trans* rather than *cis*. The evidence for this fact is given below.

CHART I



The observed chemical shifts and, where appropriate, the coupling constants of the methine protons for adducts **1–13** are listed in Table I. Deuteriochloroform was used as the solvent for the nmr studies.

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[1] H. W. Heine and R. E. Peavy, *Tetrahedron Letters*, 3123 (1965).

[2] A. Padwa and L. Hamilton, *ibid.*, 4363 (1965).

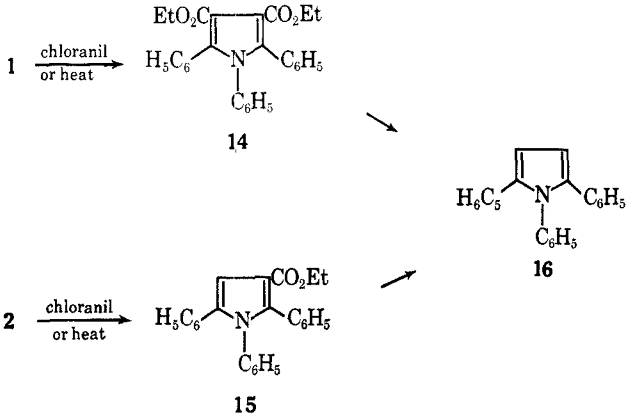
[3] R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *ibid.*, 397 (1966).

Table I

Chemical Shifts and Coupling Constants of Methine Protons

| Adduct | δ, ppm from $(CH_3)Si_4$ $H_2$ | $H_3$ | $H_4$ | $H_5$ | Cps $J_{2,3}$ | $J_{4,5}$ |
|---|---|---|---|---|---|---|
| **1** | 6.28 | ... | ... | 6.28 | ... | ... |
| **2** | 6.10 | ... | ... | 6.10 | ... | ... |
| **3** | 6.77 | ... | ... | 6.77 | ... | ... |
| **4** | 6.22 | ... | ... | 6.22 | ... | ... |
| **5** | 6.22 | ... | ... | 6.22 | ... | ... |
| **6** | 6.70 | ... | ... | 6.70 | ... | ... |
| **7** | 5.70 | 4.69 | 4.73 | 5.60 | 2.5 | 2.5 |
| **8** | 5.78 | 3.57 | 3.57 | 5.78 | 1.2 | 1.2 |
| **9** | 5.62 | 3.69 | 3.69 | 5.90 | 8 | 8 |
| **10** | 5.67 | 4.22 | 3.67 | 5.92 | 10 | 1.2 |
| **11** | 5.62 | 3.96 | 3.40 | 5.82 | 10 | 1.2 |
| **12** | 5.77 | 4.14 | 3.53 | 5.91 | 10 | 1.2 |
| **13** | 6.90 | ... | ... | 6.90 | ... | ... |

Evidence that carbon–carbon cleavage of the aziridine ring had occurred in the reaction between 1,2,3-triphenylaziridine and ethyl acetylene dicarboxylate and ethyl propiolate was obtained by conversion of the adducts to known pyrroles. Thus, the adducts 1,2,5-triphenyl-3,4-dicarbethoxy-3-pyrroline (**1**) and 1,2,5-triphenyl-3-carbethoxy-3-pyrroline (**2**) were oxidized by chloranil to the corresponding 1,2,5-triphenyl-3,4-dicarbethoxypyrrole (**14**) and 1,2,5-triphenyl-3-carbethoxypyrrole (**15**) which in turn were saponified and decarboxylated to 1,2,5-triphenylpyrrole (**16**). Furthermore, an authentic sample of **15** was synthesized by reaction of ethyl 2,3-dibenzoylpropanoate and aniline.[4] Conversion of **1** into **14** and **2** into **15** was also achieved by heating the 3-pyrrolines in dodecane.



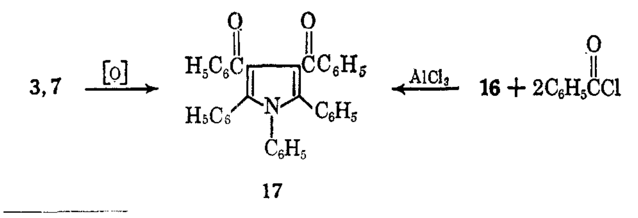
**14**

**16**

**15**

$C_6H_5COCH_2CH_2(CO_2C_2H_5)COC_6H_5 + C_6H_5NH_2 \longrightarrow$ **15**

Proof that demonstrated carbon–carbon cleavage of the aziridine ring in the reaction between 1,2,3-triphenylaziridine with dibenzoylacetylene involved the oxidation of the adduct **3** to 1,2,5-triphenyl-3,4-dibenzoylpyrrole (**17**). Since **17** is a new compound it was unambiguously synthesized by a Friedel–Crafts reaction of 1,2,5-triphenylpyrrole (**16**) and benzoyl chloride.



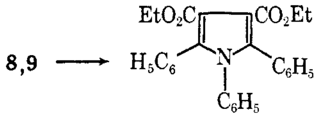
**17**

The nmr spectra of **1–6** in deuteriochloroform also disclosed that carbon–carbon cleavage of the aziridine ring had occurred and that the adducts were 3-pyrrolines rather than 2-pyrrolines. Compounds **1–6** exhibited a single resonance peak (besides those of the aromatic protons) that would be assigned to the methine group (Table I). The nmr spectrum of a 2-pyrroline would have had at least two peaks corresponding to two nonequivalent protons.

The isolation of the 3-pyrrolines in excellent yield is of interest since they seem to be only transient intermediates in the reaction of 2-aroylaziridines with dimethylacetylene dicarboxylate.[2]

The structure of the adduct **7** was elucidated by a molecular weight determination and oxidation to **17**. The stereochemistry of **7** was determined by an nmr study. The coupling constants are consistent with the Karplus correlation[5] and the observed values are in good agreement with those calculated by applying the Karplus equation to the dihedral angles measured on Dreiding models. On the basis of the obtained data the stereoisomeric configurations as illustrated for **7** could be assigned.

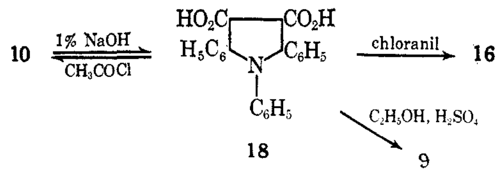
The adducts **8** and **9** were shown to be isomeric by analyses and by molecular weight determinations. Both **8** and **9** were converted by oxidation with 2,3-dichloro-5,6-dicyanoquinone to 1,2,5-triphenyl-3,4-dicarbethoxypyrrole (**14**).



**14**

The nmr spectra indicate that the stereochemical integrity of ethyl fumarate was preserved in the adduct **8** but that in the case of ethyl maleate an inversion at $C_3$ had taken place. The chemical shifts and the coupling constants show that the protons at $C_2$ and $C_3$ are *cis* and the protons at $C_4$ and $C_5$ are *cis*. Although a structure can be proposed where all four hydrogens are *cis* to each other it seems more likely that the structure as shown in **9** is the actual configuration.

The structure of the adduct of 1,2,3-triphenylaziridine with maleic anhydride was shown to be **10** by its saponification to 1,2,5-triphenylpyrrolidine-3,4-dicarboxylic acid (**18**). Conversion of **18** by aromatization and decarboxylation to **16** completed the structural proof. The crude **18** could also be reconverted to **10** by reaction with acetyl chloride or esterified to form **9**.



The structure of the adduct of 1,2,3-triphenylaziridine with N-phenylmaleimide was shown to be **12** by an alternate synthesis. Reaction of **10** with aniline gave the amide **19** which reacted with acetic anhydride to yield **12**.

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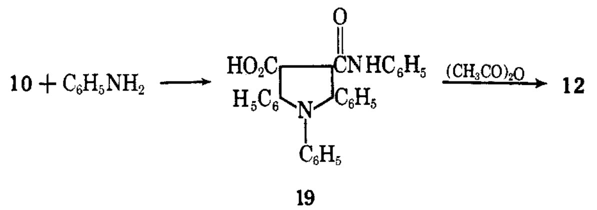
[4] S. Kapf and C. Paal, *Ber.*, **21**, 3053 (1888).

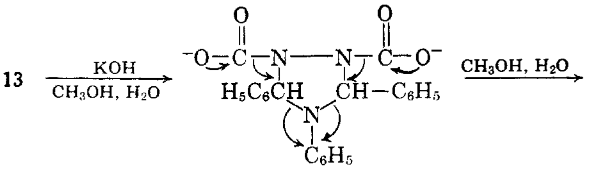
[5] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).



19

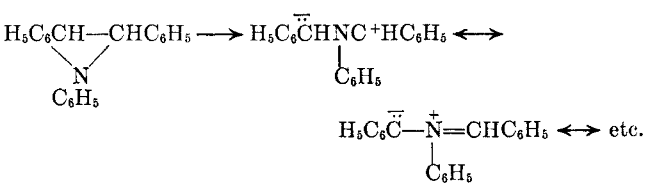
The configurations of 10–12 were assigned by an examination of the nmr spectra (Table I). The assignments were based on the assumption that $J_{cis} > J_{trans}$, on observed chemical shifts, band areas, and coupling constants (again in agreement with the Karplus equation).

The structure of 13 was proved by its nmr spectrum (a single resonance peak for the methine protons) and by a novel decarboxylative elimination. Treatment of 13 with methanolic potassium hydroxide gave benzalazine in 77% yield and aniline. Benzalazine was possibly produced by the following scheme.



$$2CO_2 + C_6H_5CH{=}N{-}N{=}CH{-}C_6H_5 + C_6H_5NH_2$$

The reaction of the aziridines with alkenes and alkynes may involve the formation of a 1,3-dipole intermediate[3] which subsequently adds to the unsaturated substrate



A 1,3-diradical intermediate may be possible and cannot be ruled out at this time.

## Experimental Section

**1,2,5-Triphenyl-3,4-dicarbethoxy-3-pyrroline** (1).—A mixture of 1.98 g of 1,2,3-triphenylaziridine[6] and 1.29 g of diethylacetylene dicarboxylate in 50 ml of dry toluene was refluxed for 4 hr. The mixture was cooled and the solvent was evaporated to give 3.15 g (97%) of crude 1. Three recrystallizations from toluene and petroleum ether (bp 35–60°) 1:10, v:v), gave 1, mp 180–181°.

*Anal.* Calcd for $C_{28}H_{27}NO_4$: C, 76.30; H, 6.26; N, 3.30. Found: C, 76.17; H, 6.16; N, 3.17.

**1,2,5-Triphenyl-3-carbethoxy-3-pyrroline** (2).—A mixture of 257 mg of ethyl propiolate and 626 mg of 1,2,3-triphenylaziridine in 15 ml of toluene was refluxed for 13 hr. The solvent was removed to give a quantitative yield of 2. Recrystallization of 2 from absolute ethanol gave product melting at 161–162°.

*Anal.* Calcd for $C_{25}H_{23}NO_2$: C, 81.28; H, 6.27; N, 3.79. Found: C, 80.96; H, 6.72; N, 3.80; mol wt, 369.[7]

**1,2,5-Triphenyl-3,4-dibenzoyl-3-pyrroline** (3).—A mixture of 272 mg of 1,2,3-triphenylaziridine and 225 mg of dibenzoylacetylene in 10 ml of toluene was refluxed for 5 hr and cooled; the solvent was evaporated. The crude product (450 mg, 93%) was recrystallized from a toluene–petroleum ether mixture (1:10). The recrystallized 3 melted at 260–265°.

*Anal.* Calcd for $C_{36}H_{27}NO_2$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.60; H, 5.79; N, 2.86.

**1,2,5-Triphenyl-3,4-bis(trifluoromethyl)-3-pyrroline** (4).—Hexafluoro-2-butyne was bubbled into a tube containing 310 mg of 1,2,3-triphenylaziridine and 5 ml of toluene. The tube was sealed and placed in an oven at 200° for 12 hr. Evaporation of the solvent gave 530 mg of crude 4. The crude 4 was purified by dissolving it in the minimum amount of methanol and adding water to the point of turbidity and cooling. Purified 4 melted at 149–150°.

*Anal.* Calcd for $C_{24}H_{17}F_6N$: C, 66.51; H, 3.95; N, 3.23. Found: C, 66.89; H, 3.74; N, 3.27.

**1-(*p*-Bromophenyl)-2,5-diphenyl-3,4-dicarbethoxy-3-pyrroline** (5).—A mixture of 298 mg of 1-(*p*-bromophenyl)-2,3-diphenylaziridine and 128 mg of diethylacetylene dicarboxylate in 10 ml of toluene was refluxed for 19 hr. Evaporation of the solvent resulted in the isolation of 428 mg (96%) of crude 5. Recrystallization from a toluene–petroleum ether mixture (1:10) gave 5, mp 171–172°.

*Anal.* Calcd for $C_{28}H_{26}BrNO_4$: C, 64.61; H, 5.03; N, 2.69. Found: C, 64.61; H, 5.05; N, 2.67.

**1-(*p*-Bromophenyl)-2,5-diphenyl-3,4-dibenzoyl-3-pyrroline** (6).—A mixture of 371 mg of 1-(*p*-bromophenyl)-2,3-diphenylaziridine and 253 mg of dibenzoylacetylene in 10 ml of toluene was refluxed for 26 hr. A crude residue of 530 mg of 6 was obtained after evaporation of the solvent. Recrystallization from a toluene–petroleum ether (1:10) gave 6 melting at 256–260°.

*Anal.* Calcd for $C_{36}H_{26}BrNO_2$: C, 73.97; H, 4.48; N, 2.40. Found: C, 73.54; H, 4.47; N, 2.57.

**1,2,5-Triphenyl-3,4-dibenzoylpyrrolidine** (**All** *trans*) (7).—A mixture of 274 mg of 1,2,3-triphenylaziridine and 230 mg of *trans*-dibenzoylethylene in 20 ml of toluene was refluxed for 18 hr. The solution was partially evaporated and filtered. The crude 7 weighed 485 mg (98%) and several recrystallizations from toluene–petroleum ether mixture gave crystals melting at 215–215.5°.

*Anal.* Calcd for $C_{36}H_{29}NO_2$: C, 85.18; H, 5.76; N, 2.76. Found: C, 84.95; H, 6.11; N, 2.84; mol wt, 507.

**1,2,5-Triphenyl-3,4-dicarbethoxypyrrolidine** (**All** *trans*) (8).—A mixture of 820 mg of diethyl fumarate and 1.26 g of 1,2,3-triphenylaziridine in 20 ml of toluene was refluxed for 10 hr. The solvent was removed and the oily residue was recrystallized from absolute ethanol. The yield of 8 was 1.5 g (73%) and it melted at 114–115°.

*Anal.* Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16. Found: C, 76.07; H, 6.70; N, 3.38; mol wt, 443.

**1,2,5-Triphenyl-3,4-dicarbethoxypyrrolidine $H_2$,$H_3$** *cis*, **$H_4$,$H_5$-** *cis* (9).—A mixture of 449 mg of 1,2,3-triphenylaziridine and 363 mg of diethyl maleate in 15 ml of toluene was refluxed for 10 hr. A crude yield of 615 mg (83%) of 9 was obtained after evaporation of the solvent. Several recrystallizations from absolute ethanol gave 9 melting at 194–195°.

*Anal.* Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.95; H, 654; N, 3.15; mol wt, 443.

**1,2,5-Triphenylpyrrolidine-3,4-dicarboxylic Andydride** (10).—A mixture of 1.70 g of 1,2,3-triphenylaziridine and 691 mg of maleic anhydride in 20 ml of *p*-xylene was refluxed for 3 hr. Evaporation of the solvent left a brown residue which was washed with petroleum ether and filtered. The 2.29 g (92%) of crude 10 was recrystallized from acetonitrile to give material melting at 214.5–215.5°.

*Anal.* Calcd for $C_{24}H_{19}NO_3$: C, 78.02; H, 5.18; N, 3.79. Found: C, 78.23; H, 5.14; N, 3.79.

**1,2,5-Triphenylpyrrolidine-3,4-dicarboximide** (11).—A mixture of 410 mg of 1,2,3-triphenylaziridine and 150 mg of maleimide in 15 ml of toluene was refluxed for 9 hr. On cooling, the fine, white needles of 11 which precipitated were collected (330 mg). Evaporation of the filtrate gave an additional 320 mg of 11. Recrystallization from toluene gave 11, mp 214–215°.

*Anal.* Calcd for $C_{24}H_{20}N_2O_2$: C, 78.23; H, 5.47. Found: C, 78.54; H, 5.52.

**1,2,5-Triphenylpyrrolidine-N-phenyl-3,4-dicarboximide** (12).—A solution of 370 mg of 1,2,3-triphenylaziridine and 240 mg of N-phenylmaleimide in 15 ml of toluene was refluxed for 5 hr. Evaporation of the solvent gave 580 mg (95%) of crude 12. Recrystallization from a toluene–petroleum ether gave 12, mp 216–218°.

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(6). T. W. J. Taylor, J. S. Owen, and D. Whittaker, *J. Chem. Soc.*, 206 (1938).

(7) The Consolidated Electrodynamic Corp. Model 103C mass spectrometer modified with a "direct introduction probe" was utilized for the determination of molecular weights listed in this paper. The temperature of the probe was at 60°. Mass spectra were obtained at ionizing voltages of 70 and 25 ev, respectively.

*Anal.* Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.38; H, 5.68; N, 6.19.

**3,4,5-Triphenyl-1,2-dicarbethxoy-1,2,4-triazolidine (13).**—A mixture of 1.48 g of 1,2,3-triphenylaziridine and 1.12 g of diethylazodicarboxylate in 40 ml of toluene was refluxed for 4 hr. An oil remained after the solvent was evaporated. The oil was taken up in a minimum of absolute ethanol. Crystals of **13** formed. Recrystallization gave 2.00 g (82%) of **13**, mp 134–134.5°.

*Anal.* Calcd for $C_{26}H_{27}N_3O_4$: C, 70.10; H, 6.11; N, 9.43. Found: C, 70.60; H, 6.20; N, 9.15; mol wt, 445.

**Oxidation of 1 to 1,2,5-Triphenyl-3,4-dicarbethoxypyrrole (14).**—A mixture of 255 mg of **1** and 173 mg of chloranil in 10 ml of *p*-xylene was refluxed for 20 hr. The reaction mixture was cooled and 60 ml of ether was added. The solution was first washed with 4% aqueous sodium hydroxide solution containing about 1% sodium bisulfite and then with water. The organic layer was dried with anhydrous sodium sulfate and filtered; the solvent was evaporated. The residue was recrystallized from absolute ethanol to give 231 mg (91%) of **14**, mp 142–143°.

*Anal.* Calcd for $C_{28}H_{25}NO_4$: C, 76.52; H, 5.73; N, 3.19. Found: C, 76.17; H, 5.93; N, 3.27; mol wt, 439.

Oxidation of **1** to **14** also occurred by refluxing a mixture of 488 mg of **1** in 15 ml of commercial dodecane for 7.5 hr. Upon cooling 426 mg (87%) of crude **1** deposited.

**Conversion of 14 into 1,2,5-Triphenylpyrrole (16).**—A mixture of 440 mg of **14** and 310 mg of potassium hydroxide in 50 ml of 97% aqueous dimethyl sulfoxide was heated with stirring at 80° for 2 hr. The solution was cooled and the resultant precipitate was dissolved in 100 ml of water. The clear solution was acidified with 5 ml of concentrated hydrochloric acid and the precipitate was filtered to give 260 mg of 1,2,5-triphenyl-3,4-dicarboxylic acid pyrrole.

This pyrrole (110 mg) and 20 ml of copper chromite were placed in a tube with 2 ml of freshly distilled quinoline and the mixture was heated in an oil bath to 205–210° for 3 hr. The solution was cooled; 25 ml of ether was added. After filtration, the filtrate was extracted with dilute hydrochloric acid and then water. The ether solution was dried over anhydrous sodium sulfate, filtered, and evaporated. The brown residue was recrystallized from absolute ethanol to give 30 mg of **16**, mp 229.5–232°. A mixture melting point with an authentic sample of **16** was not depressed and the infrared spectra of the two samples were identical.

**Oxidation of 2 to 1,2,5-Triphenyl-3-carbethoxypyrrole (15).**—A mixture of 130 mg of **2** and 210 mg of chloranil in 10 ml of *p*-xylene was refluxed for 9 hr and the reaction mixture was worked up as described for the oxidation of **1** to **14**. Recrystallization of the residue gave 129 mg of **15**, mp 173–174°. This corresponds to the lit.[4] mp 169–170° and mol wt 367. An alternate synthesis of **15**[4] gave identical material as isolated by the oxidation of **2**.

Oxidation of **2** to **15** occurred when a mixture of 60 mg of **2** and 6 ml of dodecane was refluxed 8 hr. Upon cooling 38 mg of **15** precipitated. Degradation of **15** into **16** was analogous to the degradation of **14** into **16**. The **16** isolated melted at 229–230°.

**The Oxidation of 3 to 1,2,5-Triphenyl-3,4-dibenzoylpyrrole (17).**—A mixture of 204 mg of **3** and 115 mg of chloranil in 10 ml of *p*-xylene was refluxed for 13 hr. The product was isolated analogously as described for the oxidation of **1** to **14**. Recrystallization from a toluene–petroleum ether mixture (1:10) gave **17**, mp 254–255°.

*Anal.* Calcd for $C_{36}H_{25}NO_2$: C, 85.86; H, 5.00; N, 2.78. Found: C, 85.40; H, 4.87; N, 2.86; mol wt, 503.

**Alternate Synthesis of 17.**—A mixture of 3.03 g of 1,2,5-triphenylpyrrole and 50 ml of carbon disulfide was placed in a flask equippped with a reflux condensor and a stirrer. The flask was placed in a cooling bath, and with stirring 3.5 g of anhydrous aluminum chloride was added. The bath was removed and a solution of 4 ml of benzoyl chloride in 8 ml of carbon disulfide was added slowly. The reaction mixture was then heated to 40° for 3 hr and cooled; water was added cautiously. The organic layer was separated and washed with 5% aqueous sodium hydroxide and water and then dried over anhydrous sodium sulfate. After filtration the solution was passed through a column containing 25 g of aluminum oxide. Elution of the product with carbon disulfide was discernible by the movement of a yellow zone through the column. Evaporation of the eluent gave 220 mg of **17**, mp 254–255°.

**Oxidation of 7 to 17.**—A mixture of 100 mg of **7** and 260 mg of chloranil in 10 ml of *p*-cymene was refluxed 9 hr. The product was isolated as described for the oxidation of **1** to **14**. A yield of 20 mg of recrystallized **17**, mp 253–254°, was obtained. A mixture melting point with an authentic sample was not depressed and the infrared spectra of the two samples were identical.

**Conversion of 10 into 16.**—A mixture of 2.54 g of **10** in 50 ml of 1% aqueous sodium hydroxide was refluxed with stirring for 2 hr. The solution was cooled and acidified with 10% hydrochloric acid. The gelatinous precipitate was filtered and dried in a vacuum oven to give the crude diacid **18**. The diacid was heated in *p*-xylene and filtered, mp 207–208.5°.

A mixture of 300 mg of crude **18** and 330 mg of chloranil in 45 ml of *p*-xylene was refluxed for 16 hr. The product was isolated by the procedure described for the oxidation of **1** to **14**. Recrystallization of the dark residue from absolute ethanol gave 80 mg of **16**.

**Esterification of 18 to 9.**—A mixture of 2.23 g of **18**, 58 ml of absolute ethanol, and 4 ml of concentrated sulfuric acid was refluxed for 20 hr. The solution was cooled and the resultant solid was filtered. Ether was added to the filtrate and the filtrate was then washed with 5% sodium bicarbonate solution and water and dried over anhyrous sodium sulfate. Filtration and evaporation of the solvent yielded a brown residue. Recrystallization of the total quantity of solid material collected from absolute ethanol gave 2.02 g of **9**, mp 191–192°.

**Alternate Synthesis of 12.**—A mixture of 340 mg of **10** and 100 mg of aniline in 10 ml of benzene was refluxed for 2 hr. The solution was cooled and filtered to give 260 mg of crude **19**, mp 195–196.5°. A mixture of 120 mg of the crude **19** and 6 ml of acetic anhydride was refluxed for 1 hr. The excess acetic anhydride was evaporated and the residue was washed with ether and filtered. Recrystallization from a toluene–petroleum ether mixture gave 50 mg of **12**, mp 216°. A mixture melting point with an authentic sample was not depressed and the infrared spectra of the two samples were identical.

**Conversion of 13 into Benzalazine and Aniline.**—A mixture of 1.38 g of **13** and 2.0 g of potassium hydroxide in 30 ml of methanol was refluxed over nitrogen for 6 hr. Water (10 ml) was added and the mixture was refluxed for an additional 4 hr. Crystals of crude benzalazine (655 mg) settled out if the solution was allowed to stand overnight. Recrystallization from methanol and water gave 240 mg of benzalazine, mp 89–91°. The filtrate of the crude reaction mixture was treated with bromine to give 150 mg of 2,4,6-tribromoaniline.

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