Reactions of dimethyl acetylenedicarboxylate. III.[1] Reactions with diamines and anthranilic acid

SUSHIL K. KHETAN AND M. V. GEORGE[2]
Department of Chemistry, Indian Institute of Technology, Kanpur, India

Received February 5, 1969

Dimethyl acetylenedicarboxylate reacts with *m*-phenylenediamine, *p*-phenylenediamine and 2,2′-diaminobiphenyl, giving rise to the corresponding bisenamines, having the furmarate geometry. These bisenamines are thermally cyclized to 4(1*H*)-quinolone derivatives and a selective mode of cyclization is observed. Anthranilic acid reacts with dimethyl acetylenedicarboxylate to give an enamine adduct which when heated in diphenyl ether undergoes cyclization to methyl 7-carboxy-3-oxo-2-indolinylidene-carboxylate. Further heating of this product results in the formation of methyl 3-oxo-2-indolinylidene-carboxylate.

Canadian Journal of Chemistry, 47, 3545 (1969)

The reaction of dimethyl acetylenedicarboxylate with amines has been investigated by several groups of workers. In general, primary amines give rise preferentially to enamines having a fumarate geometry, whereas secondary amines yield either the maleates or a mixture of both maleates and fumarates. Several factors affecting these additions have been studied in detail (1).

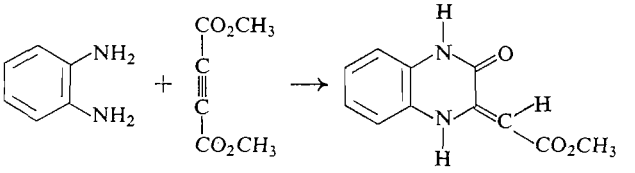
The enamine adducts obtained from the reaction of aromatic amines with dimethyl acetylenedicarboxylate, have been shown to undergo thermal cyclization, yielding 4(1*H*)-quinoline derivatives (2). Thus, when dimethyl anilinofumarate, formed from the reaction of aniline with dimethyl acetylenedicarboxylate, is refluxed in diphenly ether, it undergoes cyclization to give 2-carbomethoxy-4(1*H*)-quinolone (1*a*, 3). The object of the present investigation was to examine the reaction of dimethyl acetylenedicarboxylate with few aromatic diamines and to employ the enamine adducts formed from these reactions for the synthesis of quinoline derivatives.

The reactions of few aromatic diamines are reported in the literature. *o*-Phenylenediamine, for example, reacts with dimethyl acetylenedicarboxylate to give a cyclic product, namely, 2-oxo-3-carbomethoxymethylene-1,2,3,4-tetrahydroquinoxaline (**1**) (4). It is evident that in this reaction, the initially formed intermediate is undergoing cyclization through the attack of the second amino group, present in the starting nucleophile (Scheme I). The reaction of 2,3-diaminonaphthalene with dimethyl acetylenedicarboxylate is analogous to that of *o*-phenylenediamine (5). On the other hand, 1,8-diaminonapthalene reacts with dimethyl acetylenedicarboxylate giving rise to a mixture of products, 2-oxo-3-carbomethoxymethylene-1,2,-3,4-tetrahydronaphtho-[1,8-*ef*]-[1,4]-diazepine (**2**) and 2,3-dicarbomethoxy-1,2,3,4-tetrahydronaphtho-[1,8-*ef*]-[1,4]-diazepine (**3**) (5) (Scheme II).

In the present investigation, we have examined the reactions of *m*-phenylenediamine, *p*-phenylenediamine and 2,2′-diaminobiphenyl with dimethyl acetylenedicarboxylate. *m*-Phenylenediamine reacts with dimethyl acetylenedicarboxylate in methanol medium at room temperature to give a 69% yield of tetramethyl *m*-phenylenediaminobisfumarate (**4**). The nuclear magnetic resonance (n.m.r.) spectrum of **4** showed a sharp singlet at 4.58 τ (2H) due to the two vinylic protons. The observed position of the vinylic proton in **4** is in agreement with the reported values for anilinofumarates (1*a*). Similarly, the reaction of *p*-phenylenediamine with dimethyl acetylenedicarboxylate gave a 62% yield of tetramethyl *p*-phenylenediaminobisfumarate (**7**). Under identical conditions, the reaction of 2,2′-diaminobiphenyl gave a 96% yield of tetramethyl 2,2′-diaminobiphenylbisfumarate (**10**). The n.m.r. spectra of **7** and **10** showed the vinylic proton signals at 4.60 τ and 4.64 τ, respectively, and supports the assigned structures for these enamine adducts.

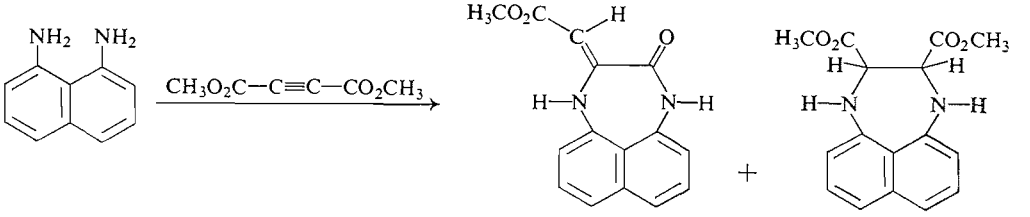
The infrared spectra of the adducts **4**, **7**, and **10** showed the presence of a hydrogen-bonded N—H, absorbing around 3280 cm^{-1}. The chelated ester carbonyl group absorption in these compounds was found to be around 1670 cm^{-1},

[1]For Part II in this series see ref. 10.
[2]To whom enquiries should be addressed.



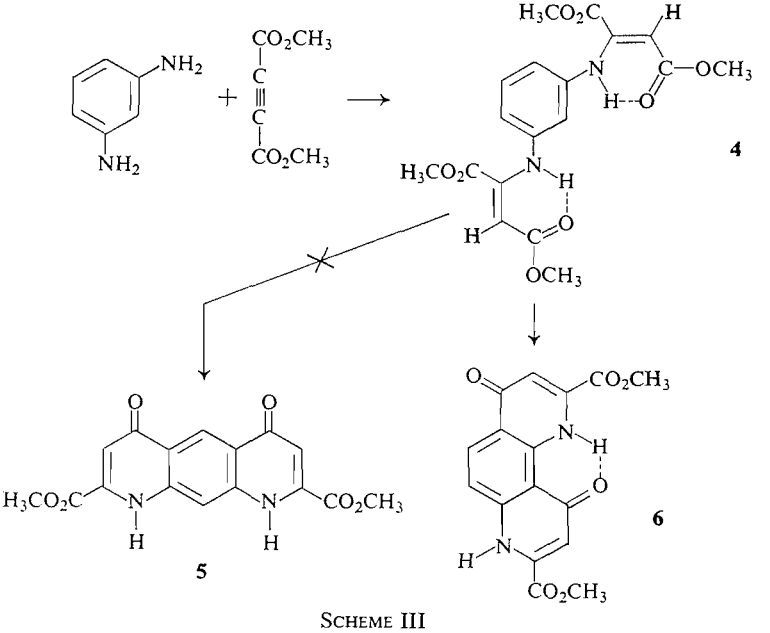
1

SCHEME I



2 3

SCHEME II

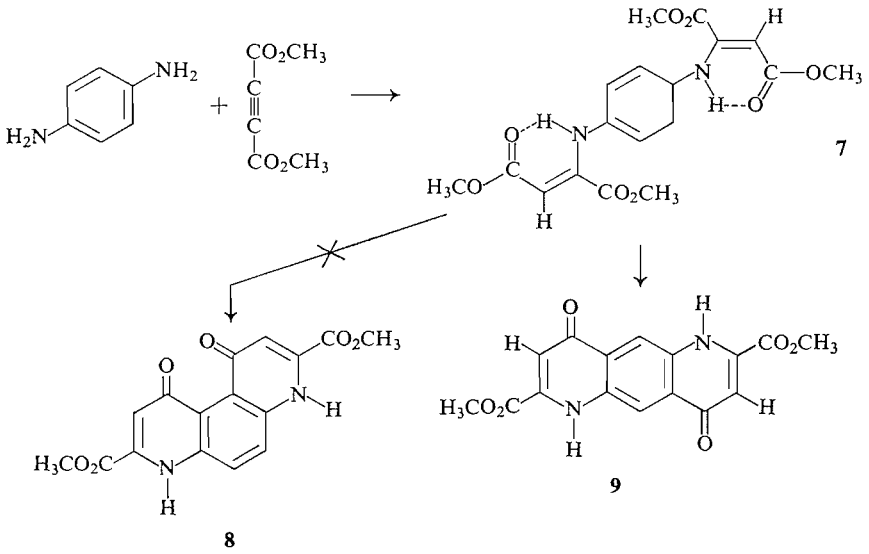


4 5 6

SCHEME III

whereas, the second ester carbonyl group appeared around 1730 cm^{-1}.

A bisenamine adduct like tetramethyl *m*-phenylenediaminobisfumarate (**4**) can undergo cyclization by two different routes giving rise to a linearly fused ring compound, 2,8-dicarbomethoxypyrido-[3,2-*g*]-quinolin-[1*H*, 9*H*]-4,6-dione (**5**) and an angularly fused ring compound, 2,8-dicarbomethoxy-1,7-[1*H*, 7*H*]-phenanthrolin-4,10-dione (**6**) (Scheme III). When the cyclization of **2** was carried out by refluxing it in diphenyl ether for 30 min, a 95% of a single product, melting at 273.5° was isolated. The structure of this product was assigned as **6**, on

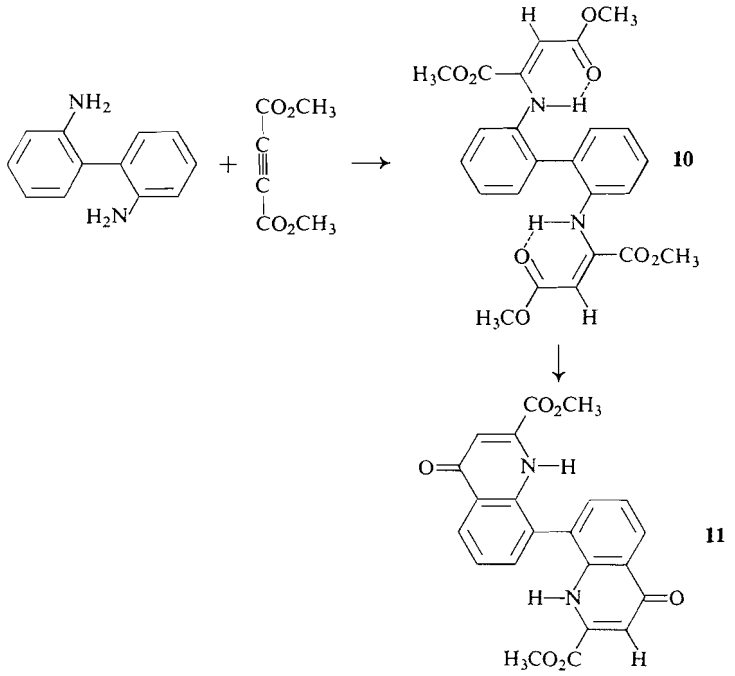


SCHEME IV

the basis of elemental analysis, molecular weight (mass spectral), and spectral evidences. The infrared spectrum of **6** showed two distinctive absorption bands at 3440 cm^{-1} and 3245 cm^{-1}, corresponding to a free and associated NH, respectively. The n.m.r. spectrum of **6**, in trifluoroacetic acid showed signals at 5.79 τ (3H) and 5.94 τ (3H), respectively, due to the ester methyl protons. In addition, the spectrum showed a symmetrical quartet centered around 1.65 τ (2H) of the AB type, with a coupling constant of 9.4 c.p.s. The appearance of this quartet is compatible only with structure **6**, in which there are two ortho protons. A coupling constant of 8–10 c.p.s. is normally observed between the two ortho protons in an aromatic ring (6). The two other olefinic protons present in the pyridone rings of **6**, appeared as two separate singlets at 1.97 τ (1H) and 3.0 τ (1H), respectively. The exact reason for the preferential formation of **6** in the cyclization of the bisenamine adduct **4**, is still not very clear.

Thermal cyclization of tetramethyl *p*-phenylenediaminobisfumarate (**7**), similarly, can give rise to two products **8** and **9**, as shown in Scheme IV. Refluxing a solution of **7** in diphenyl ether resulted in the exclusive formation (97%) of one isomer, namely, 2,7-dicarbomethoxypyrido-[2,3 *g*]-quinolin-[1*H*, 6*H*]-4,9-dione (**9**). The n.m.r. spectrum of **9** showed one singlet at 5.78 τ (6H) due to the ester methyl protons and two separate, sharp singlets at 1.56 τ (2H) and 2.57 τ (2H), respectively, due to the aromatic protons. The spectral data are in full agreement with the assigned structure **9**, for the product. If this compound were to be represented by structure **8**, one would expect the two aromatic ortho protons to appear as a quartet as in the case of **6**. Similarly, the cyclization of tetramethyl 2,2′-diaminobiphenylbisfumarate (**10**), by refluxing in diphenyl ether gave a 95% yield of 8-(2′-carbomethoxy-4′(1′*H*)-quinolonyl)-2-carbomethoxy-4(1*H*)-quinolone (**11**) (Scheme V). Confirmation of the structure **11** was derived from analytical data and spectral evidences. The n.m.r. spectrum of **11** showed a singlet at 5.90 τ (6H), assigned to the carbomethoxyl protons. In addition, the spectrum showed a complex multiplet centered around 1.67 τ (8H), due to the aromatic protons.

In an earlier paper (3), we have reported that ethyl anthranilate reacts with dimethyl acetylenedicarboxylate to give an aminofumarate which on heating undergoes cyclization to give 8-carboethoxy-2-carbomethoxy-4-(1*H*)-quinolone. In the present investigation, we have examined the reaction of anthranilic acid with dimethyl acetylenedicarboxylate with a view to studying the nature of the addition product and also of the mode of cyclization of the enamine

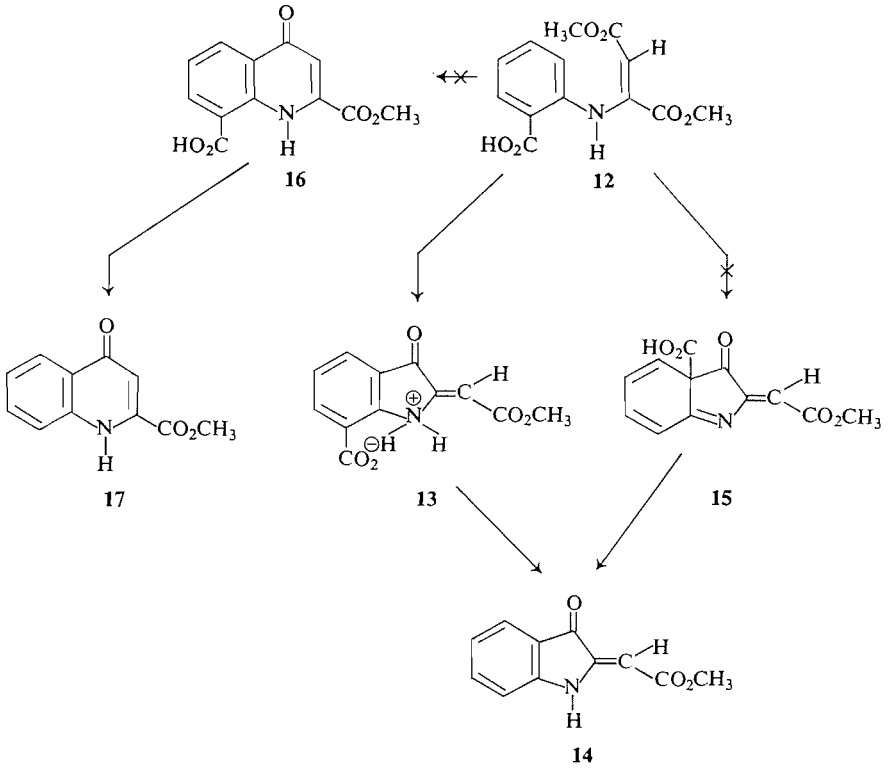


SCHEME V

adduct formed in this reaction. Treatment of anthranilic acid with dimethyl acetylenedicarboxylate in methanol gave a 78% yield of dimethyl 2-carboxyanilinofumarate (**12**). The infrared spectrum of **12** showed an absorption band at 3247 cm^{-1}, characteristic of the NH group. The two ester carbonyl group absorptions were observed at 1692 cm^{-1} and 1742 cm^{-1} respectively and the C=O absorption of the acid group was observed at 1681 cm^{-1}. The stereochemistry of **12** was inferred to be as that of a fumarate, on the basis of the vinyl proton position at 3.94 τ in its n.m.r spectrum.

When the enamine adduct **12** was heated in refluxing diphenyl ether, it gave rise to a 62% yield of a cyclized product, m.p. 264–265° (decomp.), which has been tentatively assigned the structure **13**, on the basis of analytical results and also of the following evidences. The infrared spectrum of **13** showed an ester C=O band at 1742 cm^{-1}. In addition, the spectrum showed an absorption band at 2500 cm^{-1}, characteristic of an NH_2^+ group and a second absorption band at 1620 cm^{-1}, which could be assigned to a CO_2^- group (7). The mass spectrum of **13** showed a correct molecular ion peak at 247. A second peak was observed at 229, corresponding to the loss of a water molecule from the parent compound. A similar loss of water molecule has been observed when indole-7-carboxylic acid was subjected to electron impact (8). A peak at 187, in the mass spectrum of **13**, could be assigned to the loss of a CO_2CH_3 group from the parent molecule. Other prominent peaks at mass units 171, 170, 143, 115, 114, 103, 75, 63, 39, and 28, were also observed in the spectrum of **13**.

Dry distillation of **13** (230° at 2 mm pressure) resulted in the formation of a small quantity (8.5%) of a product, melting at 137° and identified as methyl 3-oxo-2-indolinylidenecarboxylate (**14**). The yield of **15** could be improved to about 30%, by the direct dry distillation of **12**. The infrared spectrum of **14** showed a carbonyl absorption band at 1689 cm^{-1}, characteristic of a five-membered ring C=O in an indogenide system (9). In addition, the spectrum showed a second C=O absorption at 1709 cm^{-1} and an NH absorption band at 3215 cm^{-1}. The n.m.r. spectrum of **14** showed a broad signal at -1.32 τ (1H), due to the NH proton, a multiplet centered around 2.08 τ (4H) due to the aromatic protons and a sharp singlet at 6.07 τ (3H) due to the



SCHEME VI

carbomethoxy protons. In addition, the spectrum showed a doublet at 3.78 τ (1H) due to the vinylic proton, which was split by the NH proton.

Two other possible structures for the cyclized product obtained from **12** are **15** and **16** shown in Scheme VI. The infrared (i.r.) spectrum of the product which shows the presence of a broad absorption band at 2500 cm^{-1} due to the NH_2^+ group will not favor structure **15**. If structure **16**, on the other hand, correctly represents the product obtained from **12**, then we would expect this product on decarboxylation to give 2-carbomethoxy-4(1*H*)-quinolone (**17**), a known product obtained from the thermal cyclization of dimethyl anilinofumarate (1*a*). The fact that the decarboxylated product (**14**) was not identical with **17**, rules out the possibility of structure **16** for the intermediate, cyclized product.

Experimental

All melting points are uncorrected and were determined in a Thomas–Hoover melting point apparatus. Infrared (i.r.) spectra were determined in a Perkin–Elmer model 137 infrared spectrometer and ultraviolet spectra on a Cary 14-R spectrometer. Nuclear magnetic resonance traces were taken on a Varian HR-100 spectrometer, using TMS as an internal standard.

Reaction of Dimethyl Acetylenedicarboxylate with m-Phenylenediamine

A solution of *m*-phenylenediamine (1.8 g, 0.017 mole) in 10 ml of methanol was treated with a methanolic solution of dimethyl acetylenedicarboxylate (4.9 g, 0.035 mole, in 5 ml). Removal of the solvent under vacuum gave a product which on recrystallization from methanol gave 4.50 g (69%) of tetramethyl *m*-phenylenediaminobisfumarate (**4**), m.p. 146–147°.

Anal. Calcd. for $C_{18}H_{20}N_2O_8$: C, 55.10; H, 5.14; N, 7.14. Found: C, 55.34; H, 5.20; N, 7.51.

Infrared spectrum of **4** (KBr) ν_{max}: 3279 (chelated NH); 3086, 2941 (C—H); 1736 (ester C=O); 1667 (α,β-unsaturated ester C=O); 1603 (C=C), 1435, 1379 (CH_3); 1300, 1264 (C—O—C).

Ultraviolet spectrum of **4** (CH_3OH) λ_{max}: 326 mμ (ε 31 000), 243 (ε 13 800), and 225 (ε 18 200).

Nuclear magnetic resonance spectrum of **4** ($CDCl_3$): 1.07 τ (NH, 2H), 3.54 τ (phenyl, 4H); 4.56 τ (vinylic, 2H) and 6.27 τ (carbomethoxy, 12H).

2,8-Dicarbomethoxy-1,7-[1H, 7H]-phenanthrolin-4,10-dione (6)

Tetramethyl *m*-phenylenediaminobisfumarate (**4**) (1.0 g, 0.003 mole), dissolved in diphenyl ether (10 ml) was

heated in an oil bath around 250° for 30 min. Removal of the solvent and treatment of the residue with petroleum ether (60–80°) gave a product, which was recrystallized from glacial acetic acid to give 0.80 g (95%) of 2,8-dicarbomethoxy-1,7-[1*H*,7*H*]-phenanthrolin-4,10-dione (**6**), m.p. 273.5°.

Anal. Calcd. for $C_{16}H_{12}N_2O_6$: C, 58.54; H, 3.68; N, 8.53. Found: C, 58.37; H, 4.0; N, 8.69.

Infrared spectrum of **6** (KBr) ν_{max}: 3106, 2967 (CH); 1745 (ester, C=O); 1639 (ring, C=O); 1570 (C=C); 1435, 1397 (CH_3); 1271 and 1239 cm^{-1} (C—O—C).

Nuclear magnetic resonance spectrum of **6** (CH_3CO_2H): 1.86 τ (aromatic, 4H), 5.79 and 5.84 τ (carbomethoxy, 6H).

Reaction of Dimethyl Acetylenedicarboxylate with p-Phenylenediamine

A solution of *p*-phenylenediamine (1.62 g, 0.015 mole) dissolved in 10 ml of methanol was treated with a methanolic solution of dimethyl acetylenedicarboxylate (4.26 g, 0.03 mole in 5 ml). Removal of the solvent under vacuum gave a product, which on recrystallization from methanol gave 3.60 g (62%) of tetramethyl *p*-phenylenediaminobisfumarate (**7**), m.p. 129.5–130.5°.

Anal. Calcd. for $C_{18}H_{20}N_2O_8$: C, 55.10; H, 5.14; N, 7.14. Found: C, 55.14; H, 5.20; N, 7.04.

Infrared spectrum of **7** (KBr) ν_{max}: 3311 (NH); 2941 (CH); 1733 (ester, C=O); 1675 (α,β-unsaturated ester C=O); 1605 (C=C); 1433, 1383 (CH_3) and 1294, 1266 (C—O—C).

Ultraviolet spectrum of **7** (CH_3OH) λ_{max}: 348 mμ (ε 25 400) and 250 (ε 11 700).

Nuclear magnetic resonance spectrum of **7** ($CDCl_3$): 1.09 τ (NH, 2H); 3.14 τ (phenyl, 4H); 4.60 τ (vinylic, 2H); 6.27 and 6.32 τ (carbomethoxy, 12H).

2,7-Dicarbomethoxypyrido-[2,3 g]-quinolin-[1H, 6H]-4,9-dione (9)

A mixture of 1.0 g (0.003 mole) of tetramethyl *p*-phenylenediaminobisfumarate (**7**) and diphenyl ether (10 ml) was heated in an oil bath around 240–250° for 1 h. The product which separated out was filtered and treated with petroleum ether (60–80°) to give 0.83 g (97%) of impure 2,7-dicarbomethoxypyrido-[2,3 *g*]-quinolin-[1*H*,6*H*]-4,9-dione (**9**). Recrystallization of **9** from glacial acetic acid gave a pure sample, m.p. 262–263° decomp.

Anal. Calcd. for $C_{16}H_{12}N_2O_6$: C, 58.54; H, 3.68; N, 8.53. Found: C, 57.97; H, 3.80; N, 8.10.

Infrared spectrum of **9** (KBr) ν_{max}: 3344 (NH); 3106 (CH); 1712 (ester C=O); 1633 (ring C=O); 1608, 1567 (C=C); 1437, 1370 (CH_3); 1307 and 1271 cm^{-1} (C—O—C).

Nuclear magnetic resonance spectrum of **9** (CF_3CO_2H): 1.50 τ (phenyl, 2H); 2.47 τ (phenyl, 2H) and 5.78 τ (carbomethoxy, 6H).

Reaction of Dimethyl Acetylenedicarboxylate with 2,2′-Diaminobiphenyl

A mixture of 2,2′-diaminobiphenyl (1.0 g, 0.009 mole) in 10 ml of methanol was treated with a methanolic solution of dimethyl acetylenedicarboxylate (2.64 g, 0.0186 mole in 10 ml). The solvent was removed under vacuum to give 3.50 g (96%) of impure tetramethyl 2,2′-diaminobiphenylbisfumarate (**10**), which when recrystallized from a mixture (1:1) of methanol and benzene gave a pure product, m.p. 105°.

Anal. Calcd. for $C_{24}H_{24}N_2O_8$: C, 61.53; H, 5.16; N, 5.98. Found: C, 61.48; H, 5.50; N, 5.87.

Infrared spectrum of **10** (KBr) ν_{max}: 3333 (NH); 2985 (C—H); 1739 (ester C=O); 1680 (α,β-unsaturated ester C=O); 1605 (C=C), 1435, 1387 (CH_3); and 1285, 1275 (C—O—C).

Ultraviolet spectrum of **10** (CH_3OH) λ_{max}: 331 mμ (ε 26 800) and 238 (ε 23 200).

Nuclear magnetic resonance spectrum of **10** ($CDCl_3$): 1.53 τ (NH, 1H); 2.74 τ (phenyl, 8H); 4.63 τ (vinylic, 2H) and 6.40 τ (carbomethoxy, 12H).

8-(2′-Carbomethoxy-4′(1′H)-quinolonyl)-2-carbomethoxy-4(1H)-quinolone

A mixture of tetramethyl 2,2′-diaminobiphenylbisfumarate (**10**) (1.0 g, 0.0026 mole) and diphenyl ether (10 ml) was heated in an oil bath around 250° for 30 min. Removal of the solvent and treatment of the residue with petroleum ether (60–80°) gave a product, which was recrystallized from glacial acetic acid to give 0.80 g (95%) of 8-(2′-carbomethoxy-4′(1′*H*)-quinolonyl)-2-carbomethoxy-4(1*H*)-quinolone, m.p. 225–226°.

Anal. Calcd. for $C_{22}H_{16}N_2O_6$: C, 65.35; H, 3.99; N, 6.93. Found: C, 65.48; H, 4.00; N, 6.52.

Infrared spectrum of **11** (KBr) ν_{max}: 3322 (NH); 2967 (CH); 1730 (ester C=O); 1618 (ring C=O); 1575 (C=C); 1427, 1366 (CH_3); 1261 and 1227 (C—O—C).

Nuclear magnetic resonance spectrum of **11** (CF_3CO_2H): 2.52 τ (aromatic, 8H) and 5.95 τ (carbomethoxy, 6H).

Reaction of Dimethyl Acetylenedicarboxylate with Anthranilic Acid

A mixture of anthranilic acid (13.7 g, 0.1 mole) and dimethyl acetylenedicarboxylate (14.2 g, 0.1 mole) in 50 ml of methanol was stirred for 1 h. The solvent was removed under vacuum to give 21.7 g (78%) of impure dimethyl 2-carboxyanilinofumarate (**12**), which on recrystallization from methanol melted at 138°.

Anal. Calcd. for $C_{13}H_{13}NO_6$ (mol. wt., 279): C, 55.92; H, 4.69; N, 5.02. Found (mol. wt. (vapor pressure osmometry), 275): C, 55.91; H, 4.60; N, 4.97.

Infrared spectrum of **12** (KBr) ν_{max}: 3247 (NH), 1742, 1692 (ester C=O), 1681 (acid C=O), 1577 and 1499 (C=C), 1285, 1249 (O—C—O).

Ultraviolet spectrum of **13** (CH_3OH) λ_{max}: 339 mμ (ε 16 200), 238 (ε 12 800), and 218 (ε 17 900).

Nuclear magnetic resonance spectrum of **12** ($CDCl_3$): −1.11 τ (NH, 1H); 2.07, 2.66, 3.18 τ (aromatic, 4H); 4.32 τ (*trans*-vinylic, 1H); 6.17 τ and 6.22 τ (carbomethoxy, 6H).

Treatment of 2-Carboxyanilinofumarate in Diphenyl Ether at 240°

A mixture of dimethyl 2-carboxyanilinofumarate (2.0 g, 0.007 mole) and diphenyl ether (10 ml) was heated at 240° for 15 min. Removal of the solvent under vacuum and treatment of the residue with petroleum ether (60–80°) gave 1.10 g (62%) of methyl 7-carboxy-3-oxo-2-indolinylidenecarboxylate (**13**), m.p. 264–265° decomp.

Anal. Calcd. for $C_{12}H_9NO_5$ (mol. wt., 247): C, 58.30; H, 3.67; N, 5.67. Found (mol. wt. (mass spectrum), 247): C, 58.72; H, 3.78; N, 5.80.

Infrared spectrum of **12** (KBr) ν_{max}: 3125 (CH); 2500 (NH_2^+); 1742 (ester C=O); 1689 (ring C=O); 1620 CO_2^-); 1555; 1513 (C=C); 1284, 1212 (C—O—C).

Ultraviolet spectrum of **13** (CH_3OH) λ_{max}: 242 mμ (ε 17 300), 354 (ε 10 000), 373 (ε 11 600), and 219 (ε 24 200).

Decarboxylation of Methyl 7-Carboxy-3-oxo-2-indolinylidenecarboxylate (13)

Methyl 7-carboxy-3-oxo-2-indolinylidenecarboxylate (**13**) (1.0 g, 0.004 mole) was heated under reduced pressure (2 mm). A compound distilled out around 230° (2 mm), which on purification by chromatography gave 70 mg (8.5%) of methyl 3-oxo-2-indolinylidenecarboxylate (**14**), m.p. 137°.

Anal. Calcd. for $C_{11}H_9NO_3$ (mol. wt., 203): C, 65.02; H, 4.46; N, 6.89. Found (mol. wt. (vapor pressure osmometer), 203): C, 64.83; H, 4.20; N, 6.85.

Infrared spectrum of **14** (KBr) ν_{max}: 3215 (NH-associated); 1709 (ester C=O, associated); 1689 (ring C=O); 1621, 1560, and 1495 (C=C); 1274 and 1110 cm^{-1} (O—C—O).

Ultraviolet spectrum of **14** (CH_3OH) λ_{max}: 352 mμ (ε 10 200), 290 (ε 900), 278 (ε 1 200), and 243 (ε 16 000).

Nuclear magnetic resonance spectrum of **14** (CH_3CN): −1.32 τ (NH, 1H); 1.52, 2.12, and 2.59 τ (phenyl, 4H); 3.78 τ (exo-methylene, 1H) and 6.07 τ (carbomethoxy, 3H).

In a second experiment (4.2 g, 0.001 mole) dimethyl 2-carboxyanilinofumarate (**12**) was directly distilled under reduced pressure (230° at 2 mm) to give 0.90 g (30%) of **14**, m.p. 137° (mixture m.p.).

Acknowledgments

The authors thank Mr. A. H. Siddiqui for his help in Microanalysis. One of the authors (SKK) is thankful to the authorities of the Indian Institute of Technology, Kanpur for the award of a Research Assistantship.

1. (*a*) R. Huisgen, K. Herbig, A. Siegl, and H. Huber. Ber. **99**, 2526 (1966); (*b*) K. Herbig, R. Huisgen, and H. Huber. Ber. **99**, 2546 (1966); (*c*) J. E. Dolfini. J. Org. Chem. **30**, 1298 (1965); (*d*) W. E. Truce and D. G. Brady. J. Org. Chem. **31**, 3543 (1966); (*e*) E. Winterfeldt and H. Preuss. Ber. **99**, 450 (1966); (*f*) T. Y. Chen, H. Kato, and M. Ohta. Bull. Chem. Soc. (Japan), **39**, 1618 (1966); Chem. Abstr. **65**, 13633 (1966); (*g*) R. Huisgen, B. Giese, and H. Huber. Tetrahedron Letters, 1883 (1967).
2. (*a*) N. D. Heindel, T. A. Brodof, and J. E. Kogelschatz. J. Heterocyclic Chem. **3**, 222 (1966); (*b*) N. D. Heindel, I. S. Bechara, and T. F. Lemke. J. Org. Chem. **32**, 4155 (1967); (*c*) E. C. Taylor and N. D. Heindel. J. Org. Chem. **32**, 1666, 3339 (1967); (*d*) J. Reisch. Pharmazie, **22**, 420 (1967).
3. S. K. Khetan, J. G. Hiriyakkanavar, and M. V. George. Tetrahedron, **24**, 1567 (1968).
4. Y. Iwanami. Nippon Kagaku Zasshi, **82**, 778 (1961); Chem. Abstr. **58**, 11354 (1962), see, also (*a*) D. D. Chapman. J. Chem. Soc. (C), 806 (1966); (*b*) M. D. Nair and S. R. Mehta. Indian J. Chem. **6**, 490 (1968).
5. Y. Iwanami. Nippon Kagaku Zasshi, **83**, 597 (1962); Chem. Abstr. **59**, 3919 (1963).
6. L. M. Jackman. Applications of nuclear magnetic resonance in organic chemistry. Pergamon Press, London, 1959, p. 85.
7. K. Nakanishi. Infrared absorption spectroscopy, Holden-Day, Inc., San Francisco, 1962, p. 39.
8. J. C. Powers. J. Org. Chem. **33**, 2044 (1968).
9. (*a*) E. D. Hannah, G. R. Proctor, and M. A. Rehman. J. Chem. Soc. (B), 256 (1967); (*b*) D. Auld and H. G.Heller. J. Chem. Soc. (C), 680, 682 (1967).
10. S. K. Khetan and M. V. George. Tetrahedron, **25**, 527 (1969).