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REACTIONS OF DIMETHYL ACETYLENEDICARBOXYLATE—I

REACTIONS WITH PHENACYLANILINES, ETHYL ANTHRANILATE AND ANILINE

S. K. KHETAN, J. G. HIRIYAKKANAVAR and M. V. GEORGE*

Department of Chemistry, Indian Institute of Technology, Kanpur, India

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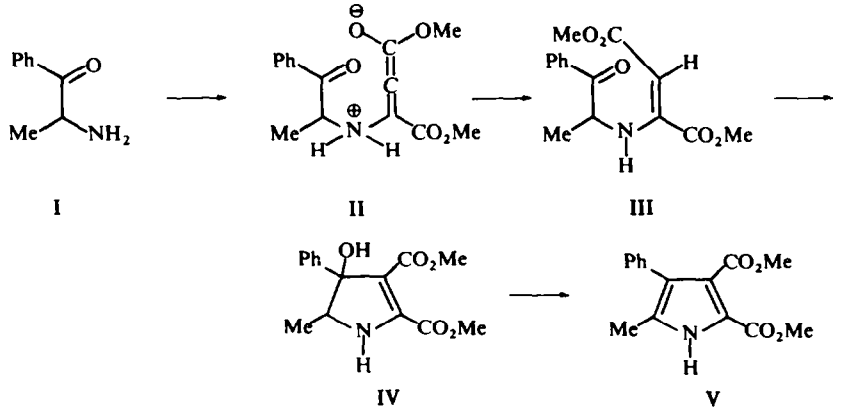
Abstract—Dimethyl acetylenedicarboxylate reacts with phenacylanilines to give Michael adducts, which undergo cyclization to pyrrole derivatives. Similarly, ethyl anthranilate and aniline react with dimethyl acetylenedicarboxylate giving rise to the corresponding fumarates which undergo cyclization under pyrolytic conditions to give 8-carbethoxy-2-carbomethoxy-4(1H)-quinolone and α-anilino-N-phenylmaleimide, respectively.

DIMETHYL acetylenedicarboxylate is known to undergo Michael additions with several nucleophiles giving rise to simple 1:1-adducts. In basic media, nucleophiles such as alkoxides,[1] phenoxides[1,2] or thiolates[3] and bisulphite[4] add to dimethyl acetylenedicarboxylate giving rise to the corresponding fumarates. Similarly, the addition of several primary and secondary amines with dimethyl acetylenedicarboxylate have been investigated and the products from these reactions are either the fumarates or compounds derived from them.[5]

In an elegant and systematic investigation, Hendrickson *et al.*[6] have shown that the reaction of nucleophiles containing suitably positioned functional groups (carbonyl or double bonds) with dimethyl acetylenedicarboxylate could provide a convenient route to synthesizing heterocyclic compounds. Thus, the reaction of an α-amino ketone, such as α-aminopropiophenone (I) with dimethyl acetylenedicarboxylate gives rise to a Michael adduct (III), which in the presence of methanolic acid undergoes cyclization to a pyrrole derivative (V). These workers have shown

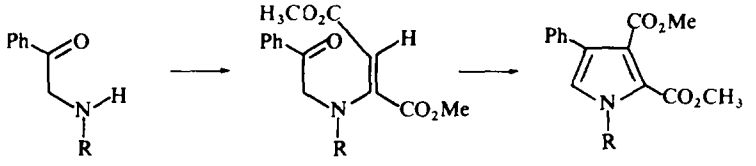


I II III IV V

* To whom enquiries should be addressed.

that the cyclization does not proceed directly from II to V, but goes through the intermediate III, by isolating this intermediate and subjecting it to further cyclization. It is interesting to note that the reactions of substances such as mercaptoacetone and ethyl mercaptoacetate with acetylene diester, lead to products arising out of a Dieckman type of cyclization and not the normal type of cyclization.[6] Winterfeldt and Dillinger[7] have recently shown that methyl N-ethyl glycinate reacts with dimethyl acetylenedicarboxylate to give dimethyl 1-ethyl-4-hydroxypyrrole-2,5-dicarboxylate. The reaction of N,N-diethyl-α-aminoacetophenone with methyl propiolate, on the other hand, gives rise to methyl 1-ethyl-4-phenylpyrrole-3-carboxylate and an interesting mechanism has been suggested to account for the formation of this pyrrole derivative.[8]

During the course of the present investigation, we have examined the reaction of a few phenacylanilines with dimethyl acetylenedicarboxylate with a view to synthesizing some 1,4-diarylpyrrole derivatives and also to study the mode of cyclization of the intermediate Michael adducts. Treatment of an equimolar mixture of phenacylaniline and dimethyl acetylenedicarboxylate in refluxing methanol gave a 53% yield of dimethyl phenacylanilinofumarate (VI).*,† Similarly, the reactions of phenacyl-*o*-methylaniline, phenacyl-*o*-ethylaniline and phenacyl-*p*-chloroaniline with dimethyl acetylenedicarboxylate gave dimethyl phenacyl-(*o*-methylanilino)fumarate (VIII), dimethyl phenacyl-(*o*-ethylanilino)fumarate (X), and dimethyl phenacyl-(*p*-chloroanilino)fumarate (XII) in 80%, 58% and 77·8% yields, respectively.



VI, R = Ph
VIII, R = *o*-CH_3—C_6H_4
X, R = *o*-C_2H_5—C_6H_4
XII, R = *p*-Cl—C_6H_4

VII, R = Ph
IX, R = *o*-CH_3—C_6H_4
XI, R = *o*-C_2H_5—C_6H_4
XIII, R = *p*-Cl—C_6H_4

Treatment of the fumarate VI with methanolic acid brought about facile cyclization to give a 21% yield of dimethyl 1,4-diphenylpyrrole dicarboxylate (VII). The poor yield of VII is due to the tendency of VI to undergo hydrolysis, under acidic conditions. Similarly, cyclizations of fumarates VIII, X and XII gave dimethyl 4-phenyl-1-(*o*-tolyl)pyrrole-2,3-dicarboxylate (IX), dimethyl 1-(*o*-ethylphenyl)-4-phenylpyrrole-2,3-dicarboxylate (XI) and dimethyl 1-(*p*-chlorophenyl)4-phenylpyrrole-2,3-dicarboxylate (XIII) in 54%, 70% and 72% yields, respectively.

We have studied the reaction of phenacyl-*p*-chloroaniline with dimethyl acetylenedicarboxylate in different solvents (under reflux) such as benzene, chloroform, tetrahydrofuran and methanol and the results are shown in Table 1. In a proton

* The stereochemistry of VI and such other Michael adducts reported in this paper have not been unequivocally established, but we assume that the addition proceeds in a trans manner leading to the fumarate, on the basis of analogy to the addition of other neucleophiles to acetylenic esters.

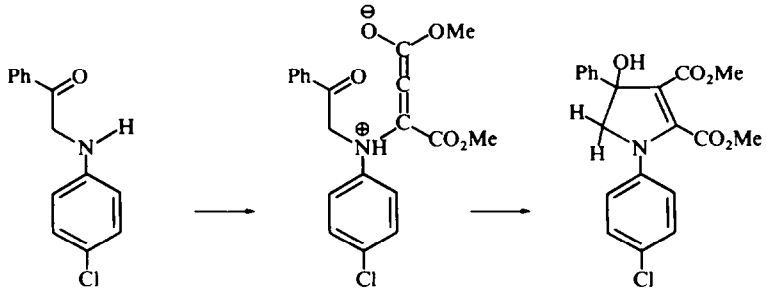
† The yields of products reported in this paper are calculated on the basis of phenacylanilines consumed in the reactions.

donating solvent like methanol, the product formed is predominantly the fumarate XII, whereas, in other aprotic solvents, such as benzene, THF and chloroform, the pyrrole derivative XIII, is obtained. It is pertinent to observe that the cyclization of the fumarate proceeds even in the absence of any catalyst, in approtic solvents

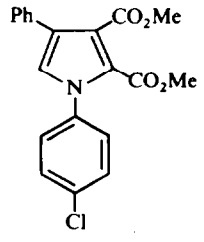
TABLE 1. REACTION OF DIMETHYL ACETYLENEDICARBOXYLATE WITH PHENACYL-*p*-CHLORO-ANILINE IN DIFFERENT SOLVENTS

Solvents	Phenacyl-*p*-chloroaniline (recovered)	XII	XIII
Tetrahydrofuran	—	—	79%
Benzene	24%	—	68·4%
Chloroform	30%	8·1%	65·3%
Methanol	12%	77·8%	12%

giving rise to the pyrrole derivative. One of the possible explanations for this observation is that the resonance stabilized anion XIV formed from the reaction of phenacyl-*p*-chloroaniline with dimethyl acetylenedicarboxylate undergoes cyclization directly to the pyrrole and not necessarily proceeding through the fumarate.



XIV



In the presence of proton donating solvents, however, the intermediate anion XIV can pick up a proton giving rise to mainly the fumarate.

The NMR spectra of these pyrrole derivatives VII, IX, XI and XIII have been examined. The vinylic proton in these compounds appeared around 3·1 τ, whereas, carbomethoxy protons were present as two distinct groups around 6·30 and 6·15 τ respectively. Of these, the low field signal (6·15 τ) is assigned to the carbomethoxy

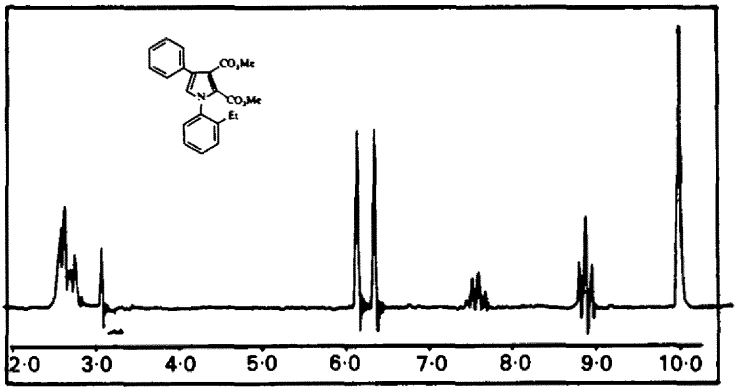
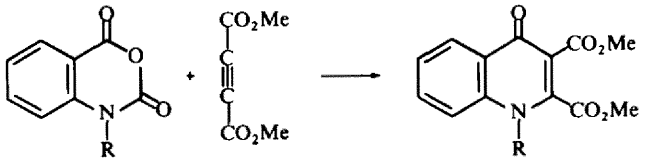


FIG. 1. NMR spectrum (100 Mc/s) of Dimethyl 1-(*o*-ethylphenyl)4-phenylpyrrole-2,3-dicarboxylate in $CDCl_3$.

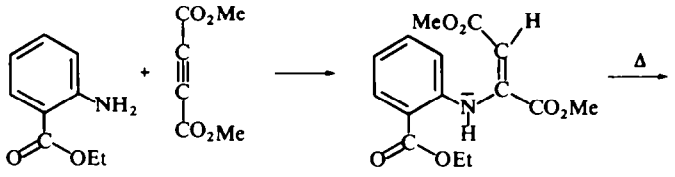
group in the 2 position of the pyrrole nuclous and the high field signal (6·35 τ) to the ester group at the 3 position. The Ph protons appear as a multiplet around 2·6 τ. A typical spectrum of one of the pyrrole derivatives (XI) is shown in Fig. 1.

The reaction of *o*-aminobenzophenone with dimethyl acetylenedicarboxylate has been reported to give a quinoline derivative.[5] Taylor and Heindel[9] have studied the reactions of several substituted *o*-aminobenzophenone and *o*-aminoacetophenones with dimethyl acetylenedicarboxylate and have shown that the yield of the quinolone derivatives depend on the basicity of the starting amino compounds. They have also examined the reactions of isotoic anhydrides with dimethyl acetylenedicarboxylate in basic methanolic medium and have obtained 4-quinolones as products.

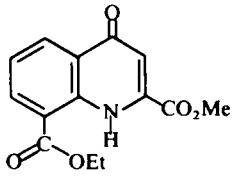


We have examined the reaction of ethyl anthranilate with dimethyl acetylenedicarboxylate, with a view to studying the mode of cyclization of the Michael adduct formed in this reaction. Refluxing an equimolar mixture of ethylanthranilate and dimethyl acetylenedicarboxylate in methanol gave a 52% yield of dimethyl 2-carbethoxyanilinofumarate (XV). Attempts to cyclize this fumarate employing methanolic acid were unsuccessful. However, when the fumarate was heated under vacuum around 250°, it gave a 70% yield of 8-carbethoxy-2-carbomethoxy-4(1*H*)-quinolone (XVI).

The IR spectrum of XVI shows an absorption band at 3311 cm^{-1}, characteristic of the NH group and the three absorption bands at 1727, 1695 and 1641 cm^{-1}, due to carbonyl absorptions. The band at 1727 cm^{-1} could be assigned to the ester C=O, the 1695 cm^{-1} band to the α,β-unsaturated ester C=O, and 1641 cm^{-1} band to the vinylogous amide C=O.[10] The NMR spectrum (Fig. 2) of XVI shows a broad NH signal at −2·32 τ (1H) and the phenyl protons appear at 1·52 and 2·65 τ



XV



XVI

(3H). The signal at 3·02 τ could be assigned to the vinylic proton (1H). The carbomethoxy protons appear as a singlet at 5·59 τ (3H), whereas the characteristic signals of the carbethoxy group are present at 5·52 (2H, quartet) and 8·56 τ (3H, triplet). The spectral data are in full agreement with the assigned structure XVI. In this connection, it might be mentioned that the thermal cyclization of the enamine adducts obtained from the reaction of anthranilonitriles and dimethyl acetylenedicarboxylate leads to the corresponding quinolone derivatives.[9]

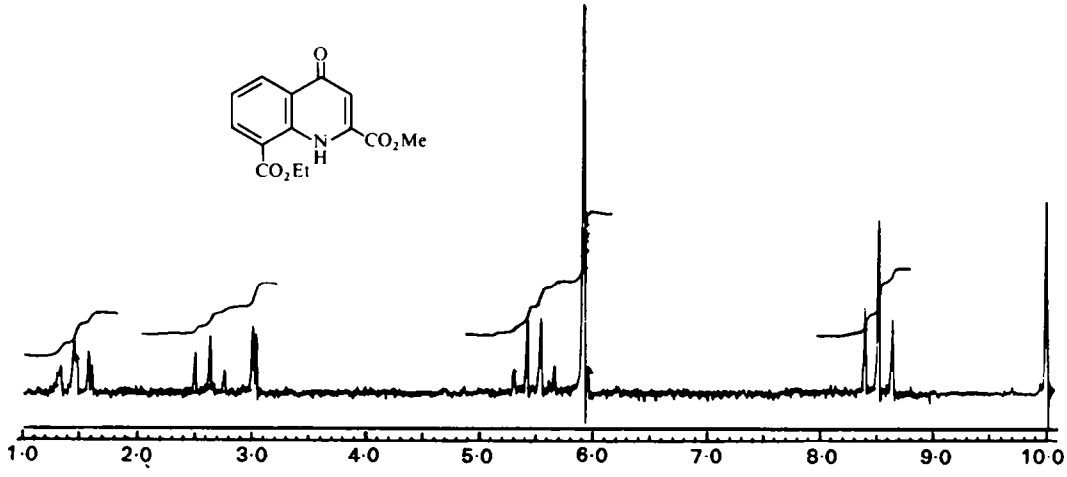
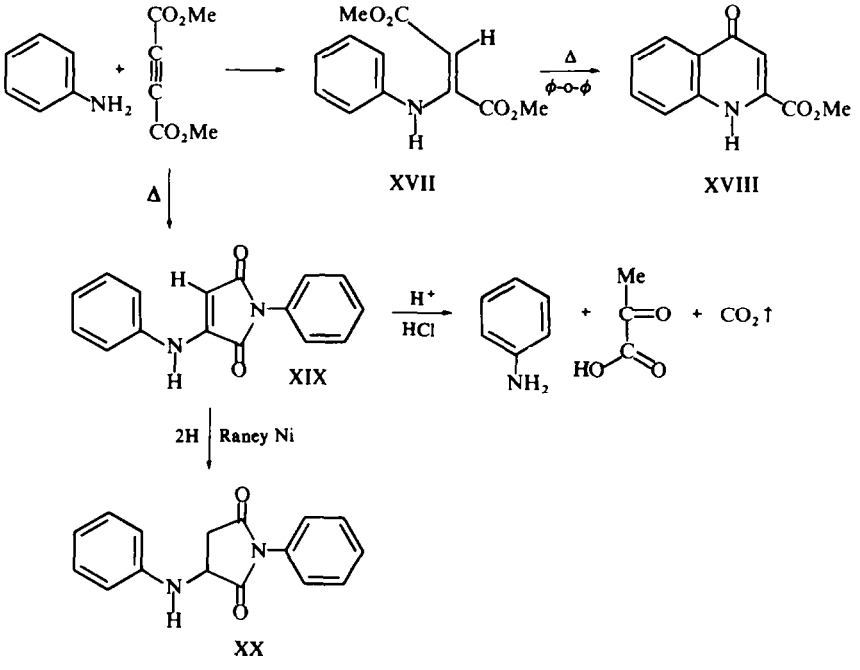


FIG. 2. NMR spectrum (60 Mc/s) of 8-Carbethoxy-2-Carbomethoxy-4(1H)-quinolone in $CDCl_3$.

In connection with our general interest in the study of the reactions of acetylenic esters, we have examined the reaction of aniline with dimethyl acetylenedicarboxylate. The reaction of aniline with dimethyl acetylenedicarboxylate is reported to give the Michael adduct, dimethyl anilinofumarate (XVII).[5e,j] This fumarate undergoes cyclization when refluxed in diphenyl ether to give 2-carbomethoxy-4(1H)-quinolone

(XVIII).[5j] We have observed that the fumarate XVII undergoes cyclization by a different route to give a poor yield (13%) of α-anilino-N-phenylmaleimide (XIX), when heated in the absence of any solvent to 150°. The yield of XIX however, could be improved (46%) when a mixture of dimethyl acetylenedicarboxylate and excess of aniline (1:2 molar ratio) was heated to the same temperature. Hydrogenation of XIX gave α-anilino-N-phenylaspartimide (XX) whereas, acid-hydrolysis of XIX gave pyruvic acid, aniline and carbon dioxide. These results are in agreement with the assigned structure for XIX.*



EXPERIMENTAL

All m.ps are uncorrected and were determined in a Thomas Hoover m.p. apparatus. IR spectra were determined on a Perkin–Elmer Model 137 Infrared spectrometer and UV spectra on a Cary 14-R spectrometer. NMR traces were taken either on a Varian A-60 or HR-100 spectrometer, using TMS as internal standard.

Reaction of dimethyl acetylenedicarboxylate with phenacylaniline. Dimethyl acetylenedicarboxylate (2 g, 0·014 mole) was slowly added to a soln of phenacylaniline (2·6 g, 0·012 mole) in abs MeOH (50 ml) over a period of 30 min. The mixture was stirred during addition and for an additional period of 1 hr. Removal of the solvent and unchanged dimethyl acetylenedicarboxylate under vacuum gave a product which was recrystallized from MeOH to give 2·3 g (53%) of VI, m.p. 148°. (Found: C, 68·06; H, 5·49; N, 3·93. $C_{20}H_{19}NO_5$ requires: C, 67·99; H, 5·38; N, 3·96%).

UV spectrum (MeOH): 244 (ε 18,720) and 290 mμ (19,060). IR spectrum (KBr): ν_{max} 1737, 1695, 1603, 1565, 1489, 1429, 1395, 1366, 1340, 1277, 1241, 1217, 1149, 997, 963, 924, 801, 768 and 696 cm^{-1}.

Dimethyl 1,4-diphenylpyrrole-2,3-dicarboxylate (VII). A soln of dimethyl phenacylanilinofumarate (1·0 g, 3 mmole) in abs MeOH (25 ml) was saturated with dry HCl gas and the mixture was refluxed for 2 hr. The solvent was removed under vacuum and the residue was treated with water. Extraction with ether gave a colourless solid which on recrystallization from MeOH gave 0·2 g (21%) of VII, m.p. 115°. (Found: C, 71·52; H, 5·22; N, 4·06. $C_{20}H_{17}NO_4$ requires: C, 71·64; H, 5·07; N, 4·10%.)

* During the course of our work, Prof. Huisgen has informed us that they have also made a similar observation concerning the formation of XIX from anilinofumarate.

UV spectrum (MeOH): 242 (ε 26,928) and 273 mμ (11,869). IR spectrum (KBr): ν_{max} 1733, 1597, 1555, 1513, 1435, 1379 and 1248 cm^{-1}. NMR spectrum ($CDCl_3$): 2·59 τ (aromatic, 10H), 3·05 (α-pyrrolyl, 1H), 6·15 and 6·03 τ (carbomethoxyl, 6H).

Reaction of dimethyl acetylenedicarboxylate with phenacyl-o-methylaniline. A soln of dimethyl acetylenedicarboxylate (1·5 g, 0·01 mole) was added to a soln of phenacyl-*o*-methylaniline (2·5 g, 0·01 mole) in abs MeOH (50 ml) and the mixture was stirred at room temp for 1 hr. Removal of the solvent gave a product which on recrystallization from MeOH gave 2·1 g (80%) of VIII, m.p. 137°. (Found: C, 68·42; H, 5·70; N, 3·80. $C_{21}H_{21}NO_5$ requires: C, 68·66; H, 5·72; N, 3·81%).

UV spectrum (MeOH): 244 (ε 17,790) and 284 mμ (21,350). IR spectrum (KBr): ν_{max} 1748, 1706, 1603, 1597, 1580, 1449, 1435, 1403, 1377, 1348, 1290, 1250, 1232, 1163, 972, 807, 774, 763 and 695 cm^{-1}.

Dimethyl 4-phenyl-1-o-tolylpyrrole-2,3-dicarboxylate (IX). Dry HCl gas was passed through a soln of dimethyl phenacyl-(*o*-methylanilino)fumarate (1 g, 0·025 mole) in 25 ml of MeOH and the mixture was refluxed for 2 hr. Removal of the solvent under vacuum, treatment of the residue with water and extraction with ether gave a product, which on recrystallization from MeOH gave 0·52 g (54%) of IX, m.p. 94°. (Found: C, 71·68; H, 5·30; N, 4·00. $C_{21}H_{19}NO_4$ requires: C, 72·02; H, 5·44; N, 4·01%).

UV spectrum (MeOH): 234 (ε 27,733) and 280 mμ (10,402). IR spectrum (KBr): ν_{max} 1724, 1504, 1435, 1374, 1279, 1242, 1198, 1136, 1111, 1047, 991, 950, 842, 767 and 695 cm^{-1}. NMR spectrum ($CDCl_3$): 2·62 τ (Ph, 9H), 3·1 τ (α-pyrrolyl, 1H), 6·15 and 6·33 τ (carbomethoxyl, 6H) and 7·91 τ (Me, 3H).

Reaction of dimethyl acetylenedicarboxylate with phenacyl-o-ethylaniline. Treatment of phenacyl-*o*-ethylaniline (1·2 g, 5 mmole) and dimethyl acetylenedicarboxylate (0·8 g, 5 mmole) in 50 ml MeOH gave 1·1 g (58%) X, which melted at 110°, after crystallization from MeOH. (Found: C, 69·07; H, 6·18; N, 3·65. $C_{22}H_{23}NO_5$ requires: C, 69·2; H, 6·03; N, 3·66%).

UV spectrum (MeOH): 244 (ε 18,070) and 285 mμ (20,890). IR spectrum (KBr): ν_{max} 1748, 1701, 1595, 1575, 1374, 1289, 1239, 1227, 974, 925, 770 and 696 cm^{-1}.

Dimethyl 1-(o-ethylphenyl)4-phenylpyrrole-2,3-dicarboxylate (XI). A soln of dimethyl phenacyl-(*o*-ethylanilino)fumarate (0·6 g, 1·6 mmole) in 50 ml of abs MeOH was saturated with dry HCl and refluxed for 2 hr. After removal of the solvent, the mixture was treated with water and extracted with ether. Work-up of the ether-extract gave 0·4 g (70%) of XI, m.p. 99°, after crystallization from MeOH. (Found: C, 72·74; H, 5·70; N, 3·83. $C_{22}H_{21}NO_4$ requires: C, 72·72; H, 5·78; N, 3·82%).

UV spectrum (MeOH): 237 (ε 23,951) and 277 mμ (9299). IR spectrum (KBr): ν_{max} 1724, 1560, 1520, 1456, 1445, 1383, 1285, 1252, 1250, 1198, 1145, 1117, 1053, 996, 952 and 840 cm^{-1}. NMR spectrum ($CDCl_3$): 2·63 τ (Ph, 9H), 3·07 τ (α-pyrrolyl, 1H); 6·35 and 6·14 τ (carbomethoxyl, 6H), 7·55 τ (methylene, 2H) and 8·89 τ (Me, 3H).

Reaction of dimethyl acetylenedicarboxylate with phenacyl-p-chloroaniline. Dimethyl acetylenedicarboxylate (3 g, 0·02 mole) was added to a soln of phenacyl-*p*-chloroaniline in abs MeOH (50 ml) and the resulting mixture was refluxed for 2 hr. Removal of the solvent and unchanged dimethyl acetylenedicarboxylate under vacuum gave a product (6·2 g) which was fractionally recrystallized from MeOH. The first crop was a small quantity (0·3 g, 12%) of unchanged phenacyl-*p*-chloroaniline, m.p. (mixture m.p.). The major product (5·8 g, 77·8%) was XII, m.p. 135° after recrystallization from MeOH. (Found: C, 61·89; H, 4·5; N, 3·58. $C_{20}H_{18}NO_5Cl$ requires: C, 61·93; H, 4·64; N, 3·61%).

UV spectrum (MeOH): 243 (ε 18,960) and 287 mμ (17,970). IR spectrum (KBr): ν_{max} 1745, 1695, 1603, 1570, 1490, 1433, 1399, 1379, 1342, 1290, 1242, 1227, 1178, 1156, 1093, 1020, 1049, 968, 925, 853, 799 and 751 cm^{-1}.

From the mother liquor, 0·4 g (12%) of XIII was isolated, m.p. 151·5°, after recrystallization from MeOH. (Found: C, 64·65; H, 4·44; N, 3·71. $C_{20}H_{16}NO_4Cl$ requires: C, 64·95; H, 4·33; N, 3·78%).

UV spectrum (MeOH): 243 (ε 29,000) and 291 mμ (7181). IR spectrum (KBr): ν_{max} 1733, 1715, 1613, 1555, 1499, 1441, 1412, 1389, 1280, 1250, 1229, 1136, 1092, 1050, 1025, 997, 945 and 848 cm^{-1}. NMR (CCl_4): 2·73 τ (Ph, 9H), 3·18 τ (α-pyrrolyl, 1H), 6·27 and 6·31 τ (carbomethoxyl, 6H).

In a subsequent run, 3 g (0·02 mole) dimethyl acetylenedicarboxylate was treated with 5 g (0·02 mole) phenacyl-*p*-chloroaniline in refluxing THF for 2 hr. Work-up of the mixture as in the previous case gave 5·9 g (79%) dimethyl 1-(*p*-chlorophenyl)4-phenylpyrrole-2,3-dicarboxylate. No fumarate could be isolated in this run.

In a similar run, employing the same amount of dimethyl acetylenedicarboxylate and phenacyl-*p*-chloroaniline, but in refluxing benzene (30 ml), a 68·4% yield of dimethyl 1-(*p*-chlorophenyl)4-phenylpyrrole-2,3-dicarboxylate and 24% of unchanged phenacyl-*p*-chloroaniline were isolated.

When the reaction of dimethyl acetylenedicarboxylate and phenacyl-*p*-chloroaniline was carried out in

refluxing chloroform, the products formed were 65·3% of XIII, and 8·1% of XII. In addition a 30% of the unchanged phenacyl-*p*-chloroaniline were also isolated.[10]

Acid-catalysed cyclization of dimethyl phenacyl-(p-chloroanilino)fumarate. A soln of dimethyl phenacyl-(*p*-chloroanilino)fumarate (1 g, 2·8 mmole) in 50 ml of MeOH was saturated with dry HCl gas and refluxed for 2 hr. Work-up of the mixture gave 0·7 g (72%) of XIII, m.p. 151·5° (mixture m.p.).

Reaction of dimethyl acetylenedicarboxylate with ethyl anthranilate. A mixture of ethyl anthranilate (3·2 g, 0·02 mole) and dimethyl acetylenedicarboxylate (2·8 g, 0·02 mole) and 20 ml MeOH, was refluxed for 2 hr. Removal of the solvent under vacuum gave a viscous liquid which was distilled under reduced press to give 3 g (52%) of XIV, b.p. 224° (0·1 mm), n_D^{22} 1·5601. (Found: C, 58·41; H, 5·0; N, 4·58. $C_{15}H_{17}NO_6$ requires: C, 58·63; H, 5·53; N, 4·56%).

UV spectrum (MeOH): 219 (ε 23,900) 236 (12,600) and 339 mμ (9881). IR spectrum (liquid film): ν_{max} 3330 (NH), 2941 (CH), 1727 and 1681 cm^{-1} (C=O). NMR spectrum ($CDCl_3$): −1·71 τ (NH, 1H), 1·62, 2·27, 2·67 and 2·99 τ (Ph, 4H), 4·53 τ (vinylic, 1H), 6·11 and 6·18 τ (carbomethoxy, 6H), 5·32 τ CH_2, 2H) and 8·57 τ (Me, 3H).

8-Carbethoxy-2-carbomethoxy-4(1H)quinolone (XV). Dimethyl 2-carbethoxyanilino-fumarate (3·07 g, 0·01 mole) was heated at 250° in an oil bath, under vacuum for 1 hr. The reaction mixture was triturated with MeOH to give a solid product which after recrystallization from EtOH gave 2 g (70%) of XV, m.p. 165°. (Found: C, 61·03; H, 4·81; N, 5·15. $C_{40}H_{30}NO_5$ requires: C, 61·08; H, 4·72; N, 5·09%).

UV spectrum (MeOH): 238 (ε 6770), 350 (11,170) and 365 mμ (14,090). IR spectrum (KBr): ν_{max} 3311 (NH), 1727, 1695 and 1641 cm^{-1} (C=O). NMR spectrum ($CDCl_3$): −2·32 τ (NH, 1H), 1·52 and 2·65 τ (Ph, 3H), 3·02 τ (vinylic, 1H), 5·59 τ (carbomethoxy, 3H), 5·52 τ (Ch_2, 2H) and 8·56 τ (Me, 3H).

In a second run, dimethyl 2-carbethoxyanilinofumarate (1·5 g, 5 mmole) in 50 ml abs MeOH was saturated with dry HCl gas and refluxed for 2 hr. Work-up yielded 1·2 g (80%) of the unchanged XIV, identified through its IR spectrum.

Reaction of dimethyl acetylenedicarboxylate with aniline. Treatment of a mixture of aniline (7 g, 00·75 mole) and dimethyl acetylenedicarboxylate (10·5 g, 00·75 mole) in MeOH (50 ml) at 0° and work-up gave 15·8 g (90%) yield of dimethyl anilinofumarate, b.p. 137° (2 mm), n_D^{22} 1·5860.

Dimethylanilinofumarate (1·2 g, 5 mmole) was heated at 150° in an oil both for 4 hr. The reaction mixture was cooled and the product was recrystallized from a mixture (1:1) of MeOH and acetone, to give 0·1 g (13%) of XVI, m.p. 236°. (Found: C, 72·63; H, 4·77; N, 10·45. $C_{16}H_{12}N_2O_2$ requires: C, 72·70; H, 4·54; N, 10·60%).

UV spectrum (MeOH): 242 (ε 26,708), 283 (7177) and 382 mμ (8132). IR spectrum (KBr): ν_{max} 3050 (NH), 1690 (C=O) and 1625 cm^{-1} (C=C).

In a second run a mixture of dimethyl acetylenedicarboxylate (3·1 g, 0·02 mole) and aniline (4 g, 0·04 mole) was heated directly to 150° for 4 hr and yielded 2·6 g (46%) of XVI, m.p. 236°.

Hydrogenation of α-anilino-N-phenylmaleimide. A soln of XVI (1 g, 3·7 mmole) in dioxan (200 ml) was hydrogenated in presence of Raney Ni at 72 psi H_2 press for 5 hr. Removal of the catalyst and the solvent gave a product which on recrystallization from benzene gave 0·5 g (58%) of XVII, m.p. 213–214° (lit.[11] m.p. 215°).

Acid-hydrolysis of α-anilino-N-phenylmaleimide. A mixture of α-anilino-N-phenylmaleimide (1·3 g, 5 mmole) and conc HCl (10 ml) was refluxed for 2 hr. Evolution of CO_2 was observerd during the hydrolysis (formation of $CaCO_3$ with lime water). The mixture was treated with water and extracted with ether. Removal of the solvent from ether extract gave 0·3 g (60%) of pyruvic acid, identified by its 2,4-dinitrophenyl-hydrazone (m.p. 216°). The aqueous soln was made alkaline by the addition of NaOH and was then extracted with ether to give an oil (0·4 g, 89%), identified as aniline through its aniline hydrochloride (m.p. 198°).

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* See footnote † on page 1568.

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