Addition Reactions of Heterocyclic Compounds. Part LX.[1] Reactions of 2-Substituted Pyridines with Acetylenic Esters leading to Quinolizines and Pyrrolo[2,1,5-*cd*]indolizines

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The reaction of methyl (2-pyridyl)acetate with methyl propiolate gave quinolizine derivatives; (2-pyridyl)acetone and 1-(2-pyridyl)butan-2-one reacted similarly. 2-Acetylpyridine and ethyl pyridine-2-carboxylate reacted with methyl propiolate to yield pyrrolo[2,1,5-*cd*]indolizines. The structures of the products were deduced mainly from their u.v. and n.m.r. spectra.

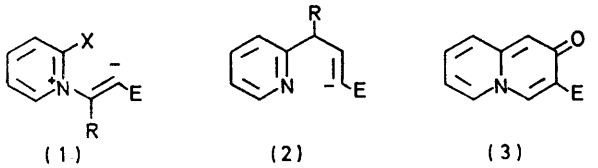
A VARIETY of compounds are formed [2] by treatment of 2-substituted pyridines with dimethyl acetylenedicarboxylate, and the reactions usually start with nucleophilic attack by the nitrogen atom,[3] or the activated 2-position,[1] on the electrophilic acetylene. The initially formed zwitterion [*e.g.* (1)] then undergoes further transformations. Methyl propiolate has been little used [4] in this type of condensation, so its reactions, along with those of the acetylenic diester, with some substituted methyl pyridines and 2-pyridylcarbonyl compounds have been investigated.

Methyl propiolate with methyl (2-pyridyl)acetate in ether gave a mixture of the quinolizines (3), (4), and (6), and the pyridine (10). Compounds (3), (4), and (10) are formed through an intermediate similar to (1). For compound (3), a 1-methoxycarbonylquinolizin-2-one structure, which could be formed by an alternative mode of cyclisation, is excluded because the deshielding effect [5] of a 1-ester group on the 8-proton is not observed in the n.m.r. spectrum, and the spectrum has the expected similarities to that of dimethyl 2-oxoquinolizine-3,4-dicarboxylate.[6] The quinolizines (3) and (4) are analogous to those obtained from acetylacetylene.[7] The u.v. and n.m.r. spectra of compound (4) under acidic conditions suggest that protonation occurs at position 3. The dihydropyridine (10) has the expected spectral similarities to (11),[8] showed a pyridinium chromophore in acid solutions, and in its n.m.r. spectrum the low-field 3-proton signal indicated the side-chain stereochemistry. The quinolizin-4-one (6), which must be formed through an intermediate of type (2), showed the characteristic very strong deshielding effect due to the 4-oxygen atom on the 6-proton, as does compound (7).[9]

The same reaction in methanol gave compounds (4) and (6), and an isomer of (4) with a similar chromophore, but undergoing protonation to give a pyridinium cation. The n.m.r. spectrum of this isomer showed signals for four aromatic protons, a low-field singlet and a higher field 3-proton system, irradiation of which at τ 6·03 caused the two-proton multiplet at τ *ca.* 5·5 to collapse to an apparent singlet. Structure (12) is compatible with these data, and is supported by the mass spectrum, which shows the loss of CO_2Me to give the base peak, but not of

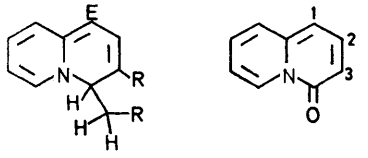
[1] Part LIX, R. M. Acheson and R. F. Flowerday, *J.C.S. Perkin I*, 1975, 394.
[2] R. M. Acheson and D. F. Nisbet, *J.C.S. Perkin I*, 1973, 1338, and earlier papers in the series.
[3] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.
[4] R. M. Acheson and M. S. Verlander, *J.C.S. Perkin I*, 1972, 1577.
[5] R. M. Acheson, J. M. F. Gagan, and R. S. Feinberg, *J. Chem. Soc.*, 1965, 948.
[6] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1968, 1629.
[7] R. M. Acheson and J. M. Woollard, *J.C.S. Perkin I*, 1975, 446.
[8] I. Dainis, *Austral. J. Chem.*, 1972, **25**, 1549.
[9] R. M. Acheson and J. N. Bridson, *J. Chem. Soc.* (*C*), 1969, 1143.

a fragment corresponding to methyl acrylate which could indicate an azepine.[10] The quinolizine (12) could



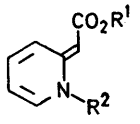
(1) (2) (3)

E = CO_2Me in all formulae

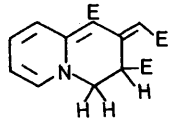


(4) R = E
(5) R = Ac

(6) 1-E, 3-*trans*-CH_a:CH_bE
(7) 1-COPh, 3-*trans*-CH_a:CH_bE
(8) 1-COEt, 3-*trans*-CH_a:CH_bE
(9) 1-COMe, 2-E

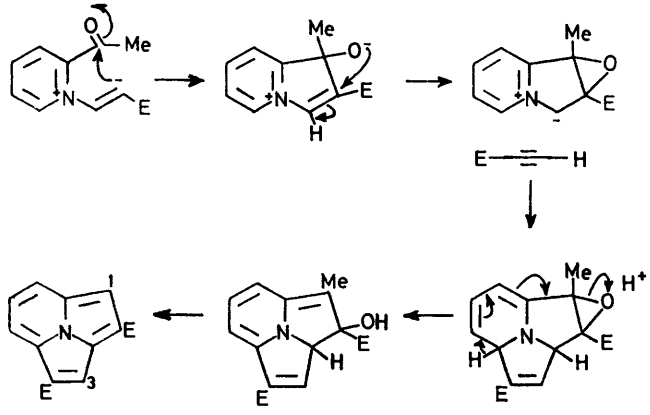


(10) R^1 = Me, R^2 = *trans*-CH_a:CH_bE
(11) R^1 = Et, R^2 = Me



(12)

be formed by protonation of a species similar to (2), cycloaddition of methyl propiolate, and hydrogen migrations.

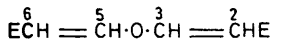


(13) 1-Me
(14) 1-CH_2E
(15) 1-OH
(16) 1-*trans*-O·CH_a:CH_bE
(17) 1-*cis*-O·CH_a:CH_bE

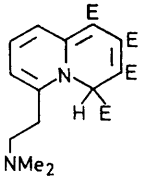
SCHEME

The quinolizin-4-one (8) was the only product from 1-(2-pyridyl)butan-2-one and methyl propiolate, and was presumably formed by addition of a second molecule of the acetylene to (2) prior to cyclisation, and the quinolizin-4-one (9) was obtained from (2-pyridyl)acetone with dimethyl acetylenedicarboxylate.

Methyl propiolate with 2-acetylpyridine gave the pyrrolo[2,1,5-*cd*]indolizine (13), and with ethyl pyridine-2-carboxylate the pyrroloindolizines (15)—(17) were formed. The pyrroloindolizines were identified by comparison of their spectral properties, notably their n.m.r spectra, with those [11] of known analogues, such as compound (14). The pyrroloindolizine (13) could be formed as indicated in the Scheme. When methanol was used as reaction solvent the vinyl ethers (18) and (19) were also obtained. The hydroxy-derivative (15) must be formed through hydrolysis of the ester group of the ethyl pyridine-2-carboxylate, and could lead to (16) and (17) by addition to more methyl propiolate. Dimethyl acetylenedicarboxylate with ethyl pyridine-2-carboxylate gave only trimethyl indolizine-1,2,3-tricarboxylate, by a process like that which occurs with 2-acetylpyridine,[12] and



(18) 2-*trans*, 5-*trans*
(19) 2-*cis*, 5-*trans*



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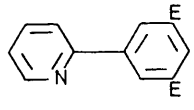

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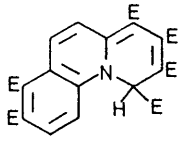

(22)

with 2-(2-dimethylaminoethyl)pyridine the 4*H*-quinolizine (20) was obtained. Trimethyl-[2-(2-pyridyl)ethyl]-ammonium iodide with methyl propiolate gave some 5-(2-pyridyl)isophthalate (21) and with dimethyl acetylenedicarboxylate a low yield of the benzoquinolizine (22).

EXPERIMENTAL

The instruments and chromotographic procedures have been described in earlier papers.[1] All analyses for new compounds were within accepted limits for C, H, and N and are available in Supplementary Publication No. SUP 21253 (5 pp.),* which also contains the i.r. and mass spectra.

Reaction of Methyl Propiolate with Methyl (2-Pyridyl)-acetate.—(i) Methyl (2-pyridyl)acetate (3·02 g) was kept with methyl propiolate (1·68 g) for 5 days at room temperature. The tar was extracted with petroleum (2 × 20 ml) and then with benzene (10 ml) to leave *methyl 2-oxoquinolizine-3-carboxylate* (3) (120 mg, 3%), yellow microneedles (from methanol), m.p. 189—192°.

The benzene extract was chromatographed twice; the elution was started with 50% petroleum–benzene. The initial fractions gave trimethyl benzene-1,3,5-tricarboxylate, and the following orange band gave *methyl* [1-(trans-2-*methoxycarbonylvinyl*)*pyridin*-2(1H)-*ylidene*]*acetate* (10) (46 mg, 1%), red needles (from methanol), m.p. 100—101·5°.

* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

[10] R. M. Acheson, J. M. F. Gagan, and D. R. Harrison, *J. Chem. Soc.* (*C*), 1968, 362.

[11] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1968, 1633.

[12] E. Winterfeldt and A. Naumann, *Chem. Ber.*, 1965, **98**, 3537.

TABLE 1

N.m.r. spectra (60 MHz; τ values, J in Hz) for solutions in deuteriochloroform with tetramethylsilane as internal reference

Compound	Proton resonances	Ester Me
(3)	1-H, 3·41; 4-H, 1·46; 6-H, 2·32d; 7-H, 3·4m; 8,9-H_2, 2·96d; [a] $J_{6,7}$ 7·0	6·13
(4)	2-H, 2·02; 4-H_a, 4·40q; 4-CH_bH_c, 7·06q, 7·66q; 6-H, 2·34d; 7-H, 3·39m; 8-H, 2·7m; 9-H, 1·33d; $J_{a,b}$ 9·3; $J_{a,c}$ 3·2; $J_{b,c}$ 16·0; $J_{6,7}$ 6·9; $J_{8,9}$ 9·3	6·23, 6·23, 6·44
(4) [b]	2-H, 1·25; 3-H, 5·66d; [c] 4-H, 4·06t; 4-CH_2, 6·79d; J 6·9; 6-H, 0·85d; 7-H, 1·95m; 8-H, 1·32m; 9-H, 2·02d; $J_{6,7}$ 6·3; $J_{8,9}$ 9	5·90 6·17, 6·17
(6)	2-H, 1·50; 6-H, 0·64d; 7-H, 2·7m; 8-H, 2·3m; 9-H, 0·77d; $J_{6,7}$ 6; $J_{8,9}$ 9; H_a, 2·27d; H_b, 3·05d, $J_{a,b}$ 15·9	6·12, 6·23
(8) [c]	2-H, 1·25; 6-H, 0·67d; 7-H, 2·46m; 8-H, 1·97m; 9-H, 0·80d; $J_{6,7}$ 6·6; $J_{8,9}$ 9·3; H_a, 2·20d; H_b, 2·98d, $J_{a,b}$ 15·6; CH_2, 6·93q; CH_2·CH_3, 8·89t, J_{Et} 7·2	6·31
(9)	3-H, 3·03; 6-H, 0·80d; 7-H, 2·75m; 8,9-H_2, 2·15—2·5m; Ac, 7·51; $J_{6,7}$ 6·9	6·09
(10)	3-H, 1·74q; 4-H, 3·3m; 5-H, 4·1m; 6-H, 3·0d; vinyl H, 5·37; $J_{3,4}$ 9·9; $J_{3,5}$ 1·2; $J_{5,6}$ 6·9; H_a, 2·43d; H_b, 4·12d, $J_{a,b}$ 13·9	6·25, 6·39
(12)	6,8-H_2, 2·50—2·85m; 7-H, 3·45t; [d] 9-H, 1·76d; vinyl H, 1·57; 3,4-H_2, 5·35—5·6, 6·0m; $J_{6,7} = J_{7,8}$ = 6·6; $J_{8,9}$ 9	6·26, 6·31, 6·48
(13)	1-Me, 7·15; 3-H, 1·97; 5-H, 1·61q; 6-H, 2·30q; 7-H, 2·06q; $J_{5,6}$ 7·5; $J_{5,7}$ 1·2; $J_{6,7}$ 8·1	6·04, 6·04
(15) [c]	3-H, 2·22; 5-H, 1·68d; 6-H, 2·16q; 7-H, 1·58d; $J_{5,6}$ 7·2; $J_{6,7}$ 8·1	6·13, 6·13
(16)	3-H, 1·80; 5-H, 1·52q; 6-H, 2·20t; 7-H, 1·96q; $J_{5,6}$ 7·2; $J_{5,7}$ 1·2; $J_{6,7}$ 8·1; H_a, 2·05d; H_b, 4·42d, $J_{a,b}$ 12	6·03, 6·03, 6·32
(17)	3-H, 1·83; 5-H, 1·54d; 6-H, 2·21t; 7-H, 1·86d; $J_{5,6}$ 7·8; $J_{6,7}$ 7·8; H_a, 2·96d; H_b, 4·76d, $J_{a,b}$ 6·6	6·03, 6·03, 6·25
(19)	2-H, 4·84d; 3-H, 3·33d; 5-H, 2·47d; 6-H, 4·35d; $J_{2,3}$ 6·6; $J_{5,6}$ 12	6·32, 6·32
(20)	4-H, 3·50; 6-CH_2, 7·05m; 7-H, 3·26d; 8-H, 2·71q; 9-H, 1·47d; CH_2·N, 7·43m; NMe_2, 7·74; $J_{7,8}$ 7·5; $J_{8,9}$ 9	6·12, 6·26, 6·33, 6·38
(20) [b]	3-H, 4·70; 4-H, 3·30; 6-CH_2·CH_2, 5·93; 7,9-H_2, 1·74d; [e] 8-H, 1·30m; NH, 1·3br; NMe_2, 6·79d, J 5	5·93, 5·93, 6·09 6·24
(21)	3,4-H_2, 2·21m; 5-H, 2·75m; 6-H, 1·28m; 2′,6′-H_2, 1·16d; 4′-H, 1·30t (J 1·7)	6·06, 6·06
(A) †	ArH_3, 2·25—3·0m; 6-H, 1·5m; keto (90%): 2-CH_2, 6·15; Me, 7·81; enol (10%): 2-CH, 4·74; Me, 8·01	
(B) ‡	ArH_3, 2·35—3·30m; CH_2·CH_3, 7·5m; CH_2·CH_3, 8·94m; keto (80%): 6-H, 1·61d, J 3·6; 2-CH_2, 6·28; enol (20%): 6-H, 1·82d, J 4·2; 2-CH, 4·84	

† (2-Pyridyl)acetone. ‡ 1-(2-Pyridyl)butan-2-one.

[a] Apparent doublet, J 3·6. [b] In trifluoroacetic acid. [c] In [$^2H_6$]dimethyl sulphoxide. [d] With further splitting. [e] Apparent doublet.

TABLE 2

U.v. spectra

Compound	Solvent [a]	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$ in parentheses)
(3)	M	234 (3·44), 245infl (2·18), 307 (1·18), 356 (0·36)
	A	225 (3·96), 294infl (0·55), 304 (0·62), 339 (0·66), 355infl (0·42)
(4)	M	212 (10·2), 261 (1·00), 266infl (0·97), 308 (1·88), 350 (0·94), 457 (0·91)
	A	215 (1·90), 307 (0·63)
(6)	M, A	214 (1·26), 236 (0·92), 245infl (0·64), 375infl (0·92), 421 (2·11), 275infl (2·66), 281 (2·88), 355infl (0·82)
	P	210 (1·69), 243 (1·46), 271infl (0·96), 317 (0·59), 353 (1·10), 375infl (0·82)
(8)	M, A	235infl (0·87), 244infl (0·71), 283 (2·63), 378 (1·14), 422 (2·21)
(9)	M	218infl (1·68), 226·5 (1·69), 255 (1·17), 370infl (0·68), 405 (1·09), 420infl (1·00)
(10)	M	208 (3·21), 252 (1·40), 299 (1·42), 425 (1·03)
	A	208 (3·08), 244infl (0·72), 269 (0·84)
(12)	M	208 (1·24), 260 (0·89), 314 (2·03), 347infl (0·90), 450 (1·31)
	A	212 (1·58), 287 (0·82)
(13)	M, A	213 (2·54), 253 (2·18), 276 (1·97), 308 (1·12), 316 (1·79), 426infl (0·84), 447 (1·08)
(15)	M, A	217 (2·25), 255 (3·16), 287infl (1·44), 310 (1·10), 319 (1·31), 332infl (0·52), 448infl (0·50), 468 (0·57)
(16)	M, A	254 (3·06), 269 (2·15), 305infl (1·03), 314 (1·45), 447 (1·23)
(17)	M, A	254 (6·04), 270 (6·49), 306infl (10·6), 314 (1·43), 448 (1·23)
(19)	M, A	252 (2·75)
(20)	M	213 (1·24), 267 (0·91), 307 (1·12), 347 (1·11), 442 (1·02)
	A	214 (1·24), 264 (0·83), 307 (1·09), 347 (0·86), 442 (0·79)
(21)	M	212 (2·58), 229 (3·40), 276 (1·19)
	A	215 (3·02), 222infl (3·95), 285 (1·45)

[a] M, methanol; A, methanol acidified with one drop of 72% perchloric acid; P, methanol–72% perchloric acid (1 : 3 v/v).

The next (yellow) band gave *methyl* 3-(trans-2-*methoxycarbonylvinyl*)-4-*oxoquinolizine*-1-*carboxylate* (6) (580 mg), yellow crystals (from methanol–chloroform), m.p. 174—177°.

The second orange band gave a mixture (1·0 g) and further elution gave only tar. The mixture was rechromatographed to give two overlapping bands. The faster-running yellow one gave more compound (6) and the slower, orange one gave *dimethyl* 4-(*methoxycarbonylmethyl*)-4H-*quinolizine*-1,3-*dicarboxylate* (4), red crystals (from methanol), m.p. 158—161°.

(ii) The experiment was repeated as before but with the addition of methanol (0·64 g, 0·02 mol). After 3 days the resulting solid was extracted with benzene (20 ml) and the extract chromatographed to give trimethyl benzene-1,3,5-tricarboxylate and compounds (4), (6), and (10). Finally a purple band was eluted with chloroform and gave *dimethyl* 3,4-*dihydro*-2-(*methoxycarbonylmethylene*)-2H-*quinolizine*-1,3-*dicarboxylate* (12) (260 mg, 8%), red crystals (from methanol), m.p. 150—153°.

Methyl 1-*Acetyl*-4-*oxoquinolizine*-2-*carboxylate* (9).—Dimethyl acetylenedicarboxylate (1·55 g) was added to (2-pyridyl)acetone [13] (1·42 g) in ether (20 ml), and the mixture was kept at 0° for 7 days. The solvent was then removed and the residue chromatographed. The first, pale yellow band gave dimethyl fumarate. The second, yellow band gave *methyl* 1-*acetyl*-4-*oxoquinolizine*-2-*carboxylate* (9) (30 mg, 1·2%), yellow plates (from methanol–ether), m.p. 133—135°.

Reaction of Methyl Propiolate with 1-(2-*Pyridyl*)*butan*-2-*one*.[13]—The pyridine (4·47 g) was mixed with methyl propiolate (5·04 g) at room temperature. After 30 min the reaction became vigorous and ether (25 ml) was added. The solvent was evaporated off and the residue chromato-

[13] J. Büchi, F. Kracher, and G. Schmidt, *Helv. Chim. Acta*, 1962, **45**, 729.

graphed to give, from a yellow-brown band, 3-(trans-2-*methoxycarbonylvinyl*)-1-*propionylquinolizin*-4-*one* (8) (182 mg), yellow needles (from methanol–chloroform), m.p. 171—173°.

Use of methanol as reaction solvent gave trimethyl benzene-1,3,5-tricarboxylate and compound (8).

Dimethyl 1-*Methylpyrrolo*[2,1,5-cd]*indolizine*-2,4-*dicarboxylate* (13).—Methyl propiolate (1·68 g) was refluxed for 22 h with 2-acetylpyridine (2·42 g). Chromatographing the tarry product on alumina gave a small amount of unchanged acetylpyridine, and from the next, yellow-brown band the *pyrroloindolizine* (13) (0·80 g, 29%), yellow microneedles (from methanol), m.p. 148—150°.

Refluxing the reactants in methanol (5 ml) for 24 h and evaporation gave a gar which was chromatographed; the first half of the first yellow band gave some 2-acetylpyridine and yellow needles (105 mg), which were shown (i.r. and n.m.r. spectra) to be a mixture of the pyrroloindolizine (13), the vinyl ether (18),[14] and trimethyl benzene-1,3,5-tricarboxylate. The second half of the first yellow band gave *dimethyl* 4-*oxahepta*-cis-2,trans-5-*dienedioate* (19) (30 mg), needles (from petroleum–toluene), m.p. 108—110°.

Reaction of Methyl Propiolate with Ethyl Pyridine-2-*carboxylate*.—The acetylene (3·36 g) was refluxed for 8 h with the pyridine (3·02 g) to give a solid tar. This was suspended in chloroform (*ca.* 20 ml) and applied to a chromatography column. The first (yellow) and second (ochre) bands both gave *dimethyl* 1-(trans-2-*methoxycarbonylvinyloxy*)*pyrrolo*[2,1,5-cd]*indolizine*-2,4-*dicarboxylate* (16) (120 mg, 2·5%), golden platelets (from methanol–chloroform), m.p. 156·6—160·5.

The next, brown band gave *dimethyl* 1-(cis-2-*methoxycarbonylvinyloxy*)*pyrrolo*[2,1,5-cd]*indolizine*-2,4-*dicarboxylate* (17) (200 mg, 2·8%), green-yellow plates (from chloroform–methanol), m.p. 167—171°.

Further elution gave only gars, but a yellow solid was left at the top of the column. This was removed and gave *dimethyl* 1-*hydroxypyrrolo*[2,1,5-cd]*indolizine*-2,4-*dicarboxylate* (15) (156 mg, 2%), yellow needles (from chloroform–methanol), m.p. 212—214°.

Reaction of Dimethyl Acetylenedicarboxylate with Ethyl Pyridine-2-*carboxylate*.—(i) The acetylene (4·26 g) was added to a solution of the pyridine (3·02 g) in ether (25 ml), and the mixture kept at 0° for 13 days. Removal of the solvent left a mobile oil which was chromatographed to give successively the unchanged acetylene, hexamethyl benzenehexacarboxylate (321 mg), and tar.

(ii) The acetylene (5·68 g) was heated with the pyridine (3·02 g) for *ca.* 15 min, until a vigorous reaction ensued. The mixture was allowed to cool to give a solid mass. Chromatography gave, from a yellow band, trimethyl indolizine-1,2,3-tricarboxylate (294 mg, 5·0%) identical (u.v., n.m.r., and i.r. spectra) with an authentic sample.[11] Further elution gave only tars.

Reaction of Dimethyl Acetylenedicarboxylate with 2-(2-*Dimethylaminoethyl*)*pyridine*.—The acetylene (2·84 g) was added to the pyridine[15] (1·50 g) [b.p. 100—102° at 20 mmHg (lit.,[16] 101—103° at 17 mmHg); n_D^{21} 1·5005] in ether (15 ml) at room temperature. After 24 h the solvent was evaporated off and the residue chromatographed. The second, orange band gave *tetramethyl* 6-(2-*dimethylaminoethyl*)-4H-*quinolizine*-1,2,3,4-*tetracarboxylate* (20) (225 mg, 5·2%), orange lumps (toluene–petroleum and 1 drop of chloroform), m.p. 146·5—148°.

The next, orange band gave yellow crystals, m.p. 86—100° (crude), probably of the 9a*H*-isomer of (20). Its n.m.r. spectrum (after the sample had been in a drying pistol) was identical with that of (20). Recrystallisation gave orange lumps, m.p. 144°, and a yellow powder, m.p. 65°, resolidifying and melting at 144°.

Trimethyl-[2-(2-*pyridyl*)*ethyl*]*ammonium Iodide*.—2-(2-Dimethylaminoethyl)pyridine (9·0 g) was refluxed with iodomethane (8·52 g) in ethanol (50 ml) for 5 h. The mixture was allowed to cool, and the iodide (16·7 g, 95%) was filtered off, giving white crystals (from aqueous methanol), m.p. 220—245° (decomp.).

Reaction of Methyl Propiolate with Trimethyl-[2-(2-*pyridyl*)-*ethyl*]*ammonium Iodide*.—The acetylene (2·52 g) was heated on a water-bath for 5 h with the pyridine (4·38 g) in dimethyl sulphoxide (20 ml). The solvent was removed and the residue washed with chloroform to leave unchanged quaternary salt. The filtrate was chromatographed. Elution of the first, pale yellow band gave a mixture of trimethyl benzene-1,3,5-tricarboxylate, m.p. 140—142°, and large lumps, m.p. 147—152°, which were separated by hand. The lumps gave *dimethyl* 5-(2-*pyridyl*)-*isophthalate* (21), yellowish rhombs (from petroleum–toluene), m.p. 154—157°; further quantities (total yield 2·5%) were obtained from the column.

Reaction of Dimethyl Acetylenedicarboxylate with Trimethyl-[2-(2-*pyridyl*)*ethyl*]*ammonium Iodide*.—The acetylene (2·84 g) was refluxed with the pyridine (2·92 g) in acetonitrile (100 ml) for 2·5 h. Evaporation and cooling gave an almost quantitative recovery of the iodide, but chromatography of the filtrate gave, from a pink band eluted with 50% ether–chloroform, hexamethyl 1*H*-benzo[*c*]quinolizine-1,2,3,4,7,8-hexacarboxylate (22) (8 mg), identical (i.r., n.m.r., and u.v. spectra) with an authentic sample.[17]

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[14] E. Winterfeldt, *Chem. Ber.*, 1964, **97**, 1952.
[15] H. E. Reich and R. Levine, *J. Amer. Chem. Soc.*, 1955, **77**, 4913.
[16] F. F. Blicke and J. L. Hughes, *J. Org. Chem.*, 1961, **26**, 3257.
[17] R. M. Acheson, M. W. Foxton, and A. R. Hands, *J. Chem. Soc.* (*C*), 1968, 387.