Addition Reactions of Heterocyclic Compounds. Part 67.[1] Products from 1-Phenylbut-1-yn-3-one with Various Heterocycles, and from Dimethyl Acetylenedicarboxylate with Some 2-Substituted Pyridines

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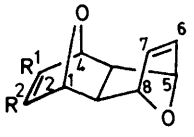
1-Phenylbut-1-yn-3-one was dimerised by 1-alkylpyrroles but with furan gave a 1 : 2 molar adduct. With 3-methylpyridine and quinoline it yielded dihydro-*H*-quinolizinones, with benzimidazole Michael addition at nitrogen occurred, but with *N*-alkylbenzimidazoles ring expansion to 1,6-benzodiazocin-2(1*H*)-ones took place. Dimethyl acetylenedicarboxylate with 1-(2-pyridyl)-butan-2-one gave a tricyclic quinolizine while quinolizines, azepines, and indolizines were obtained from other pyridines. The structures of the products were deduced from their ^{1}H, ^{13}C n.m.r., and other spectra.

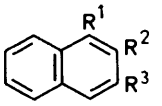
ACETYLENIC esters yield a variety of products [1,2] with simple heterocyclic compounds, but acetylenic ketones have been little investigated in this respect. Acetylacetylene undergoes Michael-type additions with pyrroles,[3] and adds to pyridines, in the presence of proton donors, to give mainly 1,4-dihydropyridine derivatives,[4] while in the absence of such donors low yields of other products are formed. A few reactions of hex-3-yne-2,5-dione with heterocyclic ylides have also been described.[5] Although methyl phenylpropiolate reacts sluggishly [6] with heterocyclic nucleophiles, 1-phenylbut-1-yn-3-one undergoes a Diels–Alder addition with cyclopentadiene,[7] additions to the triple bond,[8] and aldol condensations at the methyl group.[9] It therefore seemed likely to combine with simple heterocycles and some possibilities have now been examined. The yields in most of the reactions described are low.

RESULTS AND DISCUSSION

With furan, at 110 °C, the ketone gave a 2 : 1 molar adduct, identified as (1) from its essentially first-order 100-MHz n.m.r. spectrum, which showed that the highest-field methine protons (4a-H and 8a-H, τ 7.2) appeared as doublets (J 4.5 Hz), being coupled only to one of the adjacent methine protons. This defines the structure of the adduct; it is analogous to (2) which was obtained from dimethyl acetylenedicarboxylate.[10]



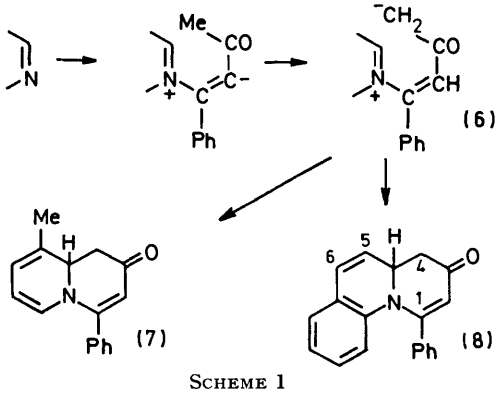
(1) R^1 = Ph, R^2 = COMe
(2) R^1 = R^2 = CO_2Me



	R^1	R^2	R^3
(3)	Ph	COMe	COMe
(4)	COMe	Ph	COMe
(5)	Ph	CO_2Et	CO_2Et

Both 1-benzyl- and 1-methyl-pyrrole only caused dimerisation of 1-phenylbut-1-yn-3-one to a naphthalene, for which structure (3) is preferred to structure (4), partially because ethyl phenylpropiolate and its derivatives yield dimers of type (5).[11] The n.m.r. spectrum of the dimer shows one very high-field methyl group, while for (4) the conformationally restricted phenyl group should affect both methyl groups. In the mass spectrometer the base peak was at $[M - 15]^+$, normal for methyl ketones, but the subsequent loss (metastable confirmed) was of water which is consistent with the postulate of adjacent acetyl groups.

3-Methylpyridine and quinoline with the acetylenic ketone gave adducts of a novel type, (7) and (8), which could be formed as indicated (Scheme 1). This is the

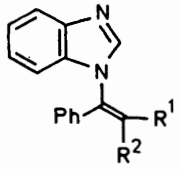


SCHEME 1

first time that a product has been observed from a heterocycle and an acetylenic ketone which requires the formation of the anion of the ketone as an intermediate (6). The n.m.r. spectra of (7) and (8) show high-field, very strongly coupled AMX systems compatible only with $>CH-CH_2$ groupings, and the loss of one methyl resonance from the reactants. Decoupling experiments for (8) enabled unambiguous assignment of the 4-, 4a-, 5-, and 6-protons, and the large (10 Hz) coupling between the 5- and 6-protons is expected of a 1,2-dihydroquinoline.[12,13] Attempts to dehydrogenate (8) by diphenyl disulphide were unsuccessful.

1-Phenylbut-1-yn-3-one with benzimidazole gave mainly (9) with some of the geometric isomer (10), while imidazole formed mixtures from which only one isomer could be isolated. The ^{1}H n.m.r. spectra for (9) and (10) were very similar, but the longer wavelength maximum in the u.v. spectrum of (9), as for (*E*)-1-phenylbut-1-en-3-one as compared with the *Z*-isomer,[14]

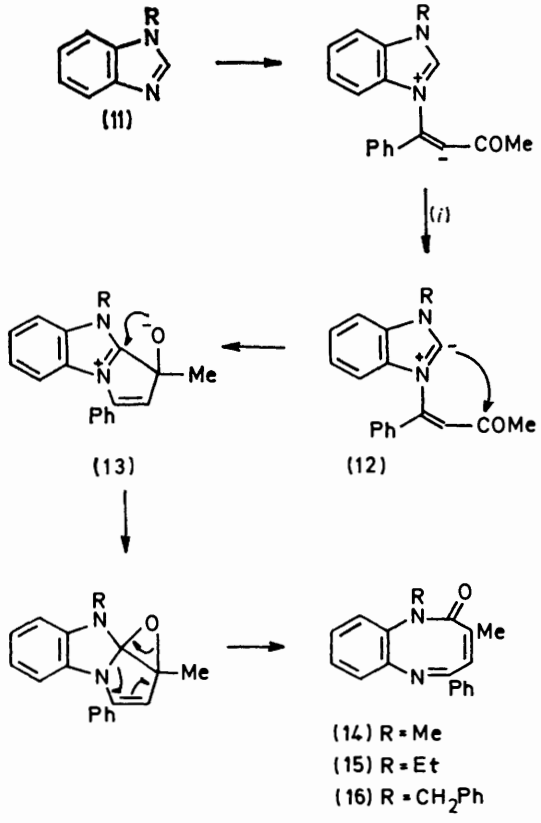
suggested the structural assignment given. 1-Methyl- and 1,2-dimethyl-imidazole gave tars with 1-phenylbut-1-yn-3-one, but three 1-alkylbenzimidazoles (11) underwent novel ring expansion (Scheme 2) to the benzodi-



(9) R^1=H, R^2=COMe (*Z*)
(10) R^1=COMe, R^2=H (*E*)

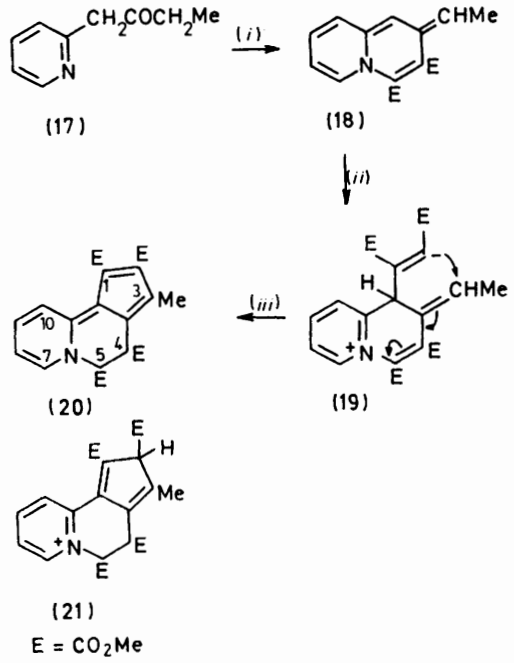
azocines (14)—(16) in low yield. The ^{1}H n.m.r. spectrum in deuteriochloroform of (14) showed a methyl group coupled with a vinylic proton, and that the *N*-methyl group had moved considerably upfield compared with that of 1-methylbenzimidazole, and was close to the positions for *NN*-dimethylacetamide (τ 6.98 and 7.06).[15] There are two low-field aromatic protons, and seven others.

On addition of Eu([$^2H_9$]fod)$_3$ the largest downfield chemical shift modification was for the *N*-methyl resonance, that of the *C*-methyl was less and the vinyl proton resonance changed least. These results are consistent with the reagent co-ordinating with the carbonyl oxygen of (14). The ^{1}H n.m.r. spectra for (15) and (16) show that the N–CH_2 protons are non-equivalent. The ^{13}C spectrum for (14) showed no sp^3 carbon



(14) R = Me
(15) R = Et
(16) R = CH_2Ph

SCHEME 2 (*i*) H^+ transfer



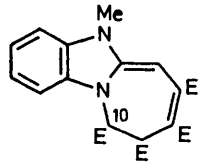
SCHEME 3 (*i*) $MeO_2CC{\equiv}CCO_2Me$, $-H_2O$. (*ii*) $Me_2OCC{\equiv}CCO_2Me$. (*iii*) Cyclisation, hydrogen shifts

atoms apart from those of the methyl groups, but resonances at δ 170.5 and 166.9. These are in the amide region and one must be due to the carbonyl carbon atom. The i.r. spectrum showed an amidic carbonyl at 1 662 cm^{-1}, while the u.v. spectrum excluded a benzimidazole system or a highly conjugated molecule.

The only type of structure compatible with this data is (14)—(16). The postulated proton exchange giving intermediate (12) is analogous to the exchange of the 2-proton of 1,3-dimethylbenzimidazolium iodide in deuterium oxide at pD 8.92,[16] and epoxy intermediates have been proposed before [17] to account for compounds formed from activated acetylenes and heterocycles. If a small amount of water was present in the reaction mixture it could attack the 2-position of the benzimidazolium intermediate (13) and the benzodiazocine system could be formed without the intermediacy of the rather strained epoxide.

1-(2-Pyridyl)butan-2-one (17) with dimethyl acetylenedicarboxylate at room temperature gave the quinolizines (20) and (26), while at higher temperature only (20) and the indolizine (29) were formed. The u.v. spectrum of (20), which showed a reversible change on acidification, was not characteristic of known 2*H*-,[18] 4*H*-, or 9a*H*-quinolizines.[19] The ^{1}H n.m.r. spectrum ($CDCl_3$) in contrast to that of (17), showed no methylene proton signals but an olefinic *C*-methyl signal and two weakly coupled aliphatic proton signals (τ 4.75 and 5.47) as special features. The lower-field resonance moved downfield when $(CD_3)_2SO$ was employed as the solvent, suggesting that it was close to the nitrogen atom. The same proton moved *ca.* τ 0.5 downfield, as does the 10-H signal of (22),[20] in trifluoroacetic acid, when

protonation probably occurs at position 2 to give (21). The added proton couples weakly with the methyl group which also moves downfield. The small coupling between the 4- and 5-hydrogen atoms of (20) is surprising, but the 2,3-proton coupling for *cis*-2-phenyl-3,6-dimethyl-2,3-dihydro-4(1*H*)-pyridone is only [21] 4 Hz and a zero coupling appears to have been observed for similar protons in some related pyridones.[22] The ^{13}C n.m.r. spectrum for (20) shows the expected Me resonances and two sp^3 carbon signals at δ 39.2 and 67.0, each bearing one hydrogen atom and assigned to the 4- and 5-C atoms respectively. The 10-C of (22) (δ 58.0) [1] and the 4-C of the quinolizine (23) (δ 65.5) [23] are the best models we have for the 5-C of (20), while the 4-C appears close to the 9-C resonance (δ 46.0) of (22), and in the expected position [1,24] for its environment. The chemical shifts for the four hydrogen-bearing aromatic carbon atoms are similar to those of the pyridone (24), and there is a satisfactory correlation between the ^{13}C resonances of (20) and (25) which was obtained as described,[25] but as an oil. Oxidation of (20) with either *N*-bromosuccinimide or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone gave a substance, not isolated, whose ^1H n.m.r. spectrum showed two low-field doublets at τ 0.44 (*J*



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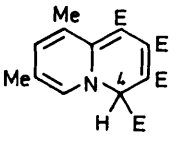

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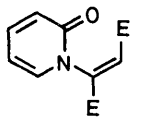

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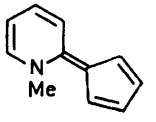
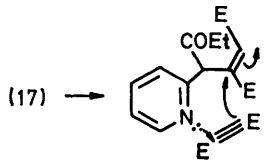


(25)

8.7 Hz) and 1.10 (*J* 9.3 Hz), assigned to the 10- and 7-H protons, respectively, and the loss of resonances at τ 4.75 and 5.47. This is consistent with the removal of the 4- and 5-protons from (20).

The disappearance of both CH_2 groups of (17) in the formation of the adduct shows that both are involved in the reaction. The postulated formation of (18) by nucleophilic attack from the nitrogen atom at the acetylene, followed by cyclisation, proton transfer, and dehydration, can easily be envisaged. Electrophilic attack on the enamine system of (18) yields (19), cyclisation and proton transfer of which lead to (20). Other schemes are of course not excluded.

The 2*H*-quinolizine (26) was identified from the similarity of its u.v. and n.m.r. spectra with those of (28),[18] the only significant difference being that the keto-group of (26) deshields the 9-proton very much less than the methyl ester grouping of (28); this could be due to a conformational preference [*e.g.* (27)]. In the mass spectrometer the molecular ion from (26) loses an ester fragment, probably from position 2, to give the base peak and an alternative fragmentation (37%) is the loss of the CH_2CO_2Me group. The ketonic carbonyl group appears in the i.r. at 1 628 cm^{-1} which can be associated



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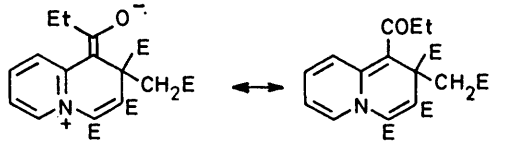
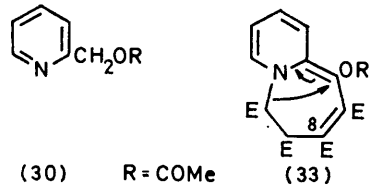


(27) (26)

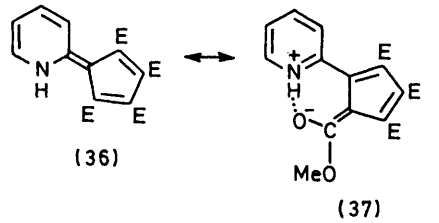
(28) (29)

with its vinylogous amidic character (27). The quinolizine could be formed from (17) and the ester in several ways, one of which is indicated.

The reactions of 2-acetoxymethyl-, 2-benzoyloxymethyl-, and 2-methoxymethyl-pyridine (30)—(32) with



(30) R = COMe (33)
(31) R = COPh (34)
(32) R = Me (35)



(36) (37)

E = CO_2Me

dimethyl acetylenedicarboxylate at 0 °C in dry ether gave the pyrido[1,2-*a*]azepines (33)—(35), which could be formed in the same way as various azepines from 2-methylbenzothiazoles [1,20] and similar compounds. The ^1H n.m.r. spectrum of (35) measured in deuteriochloroform showed a broad two-proton singlet at τ 4.44 while in CF_3CO_2H protonation at position 8 gave rise to a doublet

(τ 4.06, J 6 Hz) and a triplet (τ 5.40, J 6 Hz) which is consistent with the behaviour of (22) on protonation (Table 1). The azepines (33) and (34) were too insoluble for their ^{13}C n.m.r. spectra to be recorded. On heating in benzene both (33) and (34) gave (36). The structure of (36) follows from the similarities between its ^{13}C and ^{1}H n.m.r. spectra with those for (25), when allowance is made for a larger degree of charge separation in (36). This is highly likely as the ester groups will give additional stabilisation to negative charge in the five-membered ring [*e.g.* (37)] and bring the pyridine ring closer to the pyridinium type than in the case of (25),

The u.v. spectra, however, differ significantly, the ester groups in (36) helping resonance stabilisation (37) and preventing coplanarity of the two ring systems. Compound (36) could be formed from (33) and (34) by 1,3-shifts, as indicated, followed by elimination of the appropriate acid, and we are not aware of other instances of similar transformations with pyrido[1,2-*a*]azepines or structurally related compounds.

N.m.r. spectra measured in $CDCl_3$, with $SiMe_4$ as internal standard

(*a*) ^{1}H Spectra, measured at 60 MHz, τ (J in Hz)

Compound	Proton resonances	CO_2Me
(1) [a]	ArH(5), 2.59 (m); 1-H, 5.15 (br); 2-COMe, 7.98 (s); 4-H, 5.29 (br); 4a-H, 7.27 (q); 5-H, 5.23 (q); 6-H, 3.68 (q); 7-H, 3.60 (q); 8-H, 5.11 (q); 8a-H, 7.12 (q); J(4a,5) 4.5, J(4a,8a) 7.5; J(5,6) 1.2; J(6,7) 6.8; J(7,8) 1.2; J(8,8a) 4.5	
(3)	ArH(9), 2.45—2.80 (m); 2-COMe, 7.92 (s); 3-COMe, 7.30 (s); 4-H, 1.64 (s)	
(7)	ArH(5), 2.50 (m); 1-H_A, 7.10 (t); 1-H_B, 7.44 (m); 3-H, 4.53 (s); 6-H, 3.86 (d); 7-H, 5.08 (q); 8-H, 4.28 (d); 9-CH_3, 8.22 (s); 9a-H, 5.08 (q); J(1-H_A, 1-H_B) 16.9; J(1-H_A,9a) 16.2; J(1-H_B,9a) 4.3; J(6,7) 7.8; J(7,8) 6.0	
(8)	ArH(5), 2.35—2.70 (m); ArH(3), 3.05—3.40 (m); 2-H, 4.04 (s); 4-H_A, 6.95 (q); 4-H_B, 7.72 (q); 4a-H, 5.0 (br d); 5-H, 4.30 (q); 6-H, 3.55 (d); 8-H, 3.92 (m); J(4_A,4_B) 16.8; J(4_A,4a) 14.1; J(4_B,4a) 3.0; J(4a,5) 4.5; J(5,6) 10.0	
(9)	ArH(8), 2.45—2.90 (m); 2-H, 2.20 (s); 4-H, 2.20 (m); vinyl-H, 3.51 (s); COMe, 7.94 (s)	
(10)	ArH(8), 2.55—2.95 (m); 2-H, 2.09 (s); 4-H, 2.19 (m); vinyl-H, 3.38 (s); COMe, 8.06 (s)	
(14)	ArH(2), 1.83—2.20 (m); ArH(7), 2.38—3.18 (m); 1-Me, 6.84 (s); 3-Me, 7.99 (d); 4-H, 4.10 (q); J(3-Me,4) 1.6	
(15)	ArH(2), 2.00—2.17 (m); ArH (7), 2.48—3.11 (m); 1-CH_A, 5.82 [b]; 1-CH_B, 6.84;[b] 1-CH_2CH_3, 9.06 (t); 3-Me, 8.03 (d); 4-H, 4.17 (q); (J(1-CH_2,CH_3) 6.9; J(1-CH_A,1-CH_B) 12.6; J(3-Me,4) 1.6	
(16)	ArH(2), 2.00—2.21 (m); ArH(12), 2.42—3.10 (m); 1-CH_A, 4.91 (d); 1-CH_B, 5.50 (d); 3-Me, 7.98 (d); 4-H, 4.09 (q); J(1-CH_A, 1-CH_B) 14.4; J(3-Me,4) 1.6	
(20)	3-Me, 7.81 (s); 4-H, 5.47 (s); 5-H 4.75 (s); 7-, 9-H, 2.23—2.62 (m); 8-H, 3.29 (t); 10-H, 1.80 (d); J(7,8) 6.9; J(9,10) 8.3	6.23, 6.23, 6.31, 6.41
(20) [c]	2-H, 4.97 (q); 3-Me, 7.41 (d); 4-H, 5.07 (s); 5-H, 3.67 (s); 7-H, 1.77 (d);[a] 8-H, 2.00 (m); 9-H, 1.35 (t); 10-H, 1.15 (d)[a]; J(2,3-Me) 2.1; J(7,8) 7.8; J(9,10) 6.8	6.03, 6.18, 6.18, 6.21
(20) [c]	3-Me, 7.72 (s); 7-H, 0.62 (d);[f] 8-H, 2.51 (t);[f] 9-H, 3.04 (t);[f] 10-H, 1.18 (d); J(7,8) 9.2, J(9,10) 7.5	6.07, 6.11, 6.14, 6.16
(25)	1′-Me, 6.11 (s); 2-, 3-, 4-, 5-, 5′-H, 3.26—3.95 (m); 3′-, 4′-H, 2.48—3.03 (m); 6′-H, 2.22 (d); J(5′,6′) 9.3	
(26)	1-$COCH_2CH_3$, 7.39 (q); 1-$COCH_2CH_3$, 8.89 (t); 2-CH_2, 6.94 (s); 6-, 8-, 9-H, 3.02—3.68 (m); 7-H, 4.11 (t); J(CH_2, CH_3) 7.6; J(6,7) = J(7,8) 6.0	6.10, 6.31, 6.39, 6.50
(29)	1-$COCH_2CH_3$, 7.16 (q); 1-$COCH_2CH_3$, 8.78 (t); 5-H, 0.37 (d); 6-, 7-H, 2.28—3.09 (m); 8-H, 1.40 (d); J(CH_2,CH_3) 6.8; J(5,6) 7.6; J(7,8) 8.7	5.99, 6.10
(30) [g]	2-CH_2, 4.92 (s); 3-, 5-H, 2.75—3.05 (m); 4-H, 2.41 (t);[f] 6-H, 1.55 (d);[f] O_2CMe, 7.94 (s); J(3,4) = J(4,5) 7.5; J(5,6) 6.0	
(31)	2-CH_2, 4.36 (s); ArH(2), 1.19 (d); ArH(3), 3-, 4-, 5-H, 2.02—2.74 (m); 6-H, 1.19 (d);[f] J(5,6) 5.1	
(32) [g]	2-CH_2, 5.57 (s); 3-H, 2.71 (d); 4-H, 2.43 (m); 5-H, 2.99 (m); 6-H, 1.60 (d);[f] OMe, 6.63 (s); J(3,4) 6.6; J(5,6) 6.5	
(33)	1-, 2-, 4-H, 2.82—3.39 (m); 3-H, 3.38—4.08 (br); 6-, 7-H, 4.57 (s);[h] 10-O_2CMe, 7.90 (s)	6.20,[h] 6.29, 6.34,[h] 6.44
(34)	ArH(2), 1.71—1.90 (m); 1-, 2-, 4-H, ArH(3), 2.00—3.49 (m); 3-H, 3.87 (br); 6-, 7-H, 4.44(s) [h]	6.19,[h] 6.24, 6.35,[h] 6.46
(34) [c]	ArH(2), 1.24—1.72 (m); 1-, 2-, 3-, 4-H, ArH(3), 1.90—2.35 (m) and 2.54—3.01 (m); 6-H, 4.06 (d); 7-H, 5.40 (t); 8-H, 5.48 (d); J(6,7) 6; J(7,8) 6	6.39, 6.50, 6.60, 6.74
(35) [g]	ArH(3), 2.70—3.20 (m); 3-H, 3.75 (t); 6-, 7-H, 4.55 (s); 10-OMe, 6.52 (s); J(3,4) 6	6.12, 6.25, 6.32, 6.42
(36) [j]	ArH(2), 1.23—1.60 (m); ArH(2), 1.98—2.35 (m)	6.35, 6.35, 6.53, 6.53

(*b*) ^{13}C Spectra measured at 22.6 MHz (δ), multiplicities refer to off-resonance decoupled spectra

(14)	19.0 (q), 35.8 (q), 121.5 (d), 122.5 (d), 124.8 (d), 125.9 (d), 127.8 (d), 128.3 (d),[i] 128.5 (d),[i] 131.4 (d), 134.1 (s), 137.1 (s), 141.7 (s), 148.3 (s), 166.9 (s), 170.5 (s)	
(20) [j]	11.6 (q), 39.2 (d), 50.6 (q), 51.4 (q), 52.3 (q), 53.7 (q), 67.0 (d), 108.5 (s), 113.6 (s), 116.6 (d), 117.2 (s), 121.7 (d), 122.2 (s), 141.8 (s and d), 143.0 (d), 147.7 (s), 167.9 (s), 168.4 (s), 168.8 (s), 170.6 (s)	
(25)	46.7 (q), 111.3 (d),[i] 115.8 (d),[i] 119.3 (d), 126.2 (d), 133.9 (d), 140.2 (d), 150.2 (s) (1-C not observed)	
(36) [j]	50.7 (q),[i] 51.1 (q),[i] 114.1 (s),[i] 117.5 (s),[i] 120.1 (s), 123.1 (d), 128.7 (d), 139.5 (d), 144.0 (d), 152.2 (s), 165.4 (s),[i] 166.9 (s) [i]	

[a] Measured at 100 MHz. [b] Six lines observed. [c] Measured in trifluoroacetic acid. [d] Assignments could be reversed. [e] After oxidation with *N*-bromosuccinimide or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. [f] With further splitting. [g] Measured in tetrachloromethane. [h] Broad signal. [i] Corresponds to 2 equivalent carbon atoms. [j] Measured in $(CD_3)_2SO$.

EXPERIMENTAL

The instruments and chromatographic procedures have been described [26] but toluene was used instead of benzene for chromatography. I.r. spectra were measured in Nujol, u.v. spectra in dry methanol (M) or dry methanol acidified with 1 drop of 72% perchloric acid (A), and ^{1}H n.m.r. spectra in deuteriochloroform unless stated otherwise. 1-Phenylbut-1-yn-3-one was prepared [27] in 44% yield, b.p. 121—124 °C at 18 mmHg (lit.,[27] 120—125 °C at 14 mmHg). 1-Methyl-, 1-ethyl-, and 1-benzyl-benzimidazole were prepared by a literature method.[28]

Reactions of 1-*Phenylbut*-1-*yn*-3-*one*.—(i) *With furan*. 1-Phenylbut-1-yn-3-one (2.88 g) was heated with furan (25 ml) in a sealed tube at 110 °C for 22 h. Excess of furan was evaporated off, and chromatography of the residue gave unreacted 1-phenylbut-1-yn-3-one (1.32 g) and 2-*acetyl*-1,4,4a,5,8,8a-*hexahydro*-3-*phenyl*-1,4:5,8-trans-*diepoxynaphthalene* (1) (167 mg, 3%), irregular plates (from methanol), m.p. 166—169 °C (Found: C, 76.9; H, 5.8. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.8%), $\nu_{max.}$ 1 655, 1 619, 1 591, 1 485, and 1 441 cm^{-1}; $\lambda_{max.}$ (M), (A) 215 (ε 10 600) and 284 (7 800); *m/e* 262 (M^+, 8%), 237 (14), 212 (25), 208 (26), 184 (65), 183 (14), 171 (68), 170 (100), 169 (30), 154 (14), 144 (16), 142 (47), 141 (38), 129 (76), and 115 (58); *m** 157 (184→170), 141 (237→183), 136 (212→170), 118.5 (170→142), 115.5 (144→129), and 109.5 (184—142).

(ii) *With* N-*methyl- and* N-*benzyl-pyrrole*. 1-Phenylbut-1-yn-3-one (2.88 g) was refluxed with *N*-methylpyrrole (1.62 g) or *N*-benzylpyrrole (2.96 g) in xylene (20 ml) for 48 h. Chromatography gave unreacted 1-phenylbut-1-yn-3-one (1.60 g) followed by 2,3-*diacetyl*-1-*phenylnaphthalene* (3) (317 mg, 11%), colourless rhombs (from methanol–chloroform), m.p. 170—172 °C (Found: C, 83.3; H, 5.6. $C_{20}H_{16}O_2$ requires C, 83.2, H, 5.7%); $\nu_{max.}$ 1 698, 1 675, 1 618, 1 545, 1 444, and 1 422 cm^{-1}; $\lambda_{max.}$ (M) 215infl. (ε 26 400), 230 (38 000), 250 (35 500), 279infl. (6 900), 288 (8 100), 295infl. (6 900), 305 (1 400), and 347 (1 400); (A) 215 (2 600), 220 (6 200), 277 (6 400), 286 (7 500), and 293 nm (6 500); *m/e* 288 (M^+, 14%), 273 (100), 255 (2), 245 (2), 231 (4), 226 (3), 213 (3), and 202 (26); *m** 259 (288→273), 238 (273→255), 220 (237→245), 195.5 (273→231), 187 (273→226), and 166 (273→213).

(iii) *With* 3-*methylpyridine*. 1-Phenylbut-1-yn-3-one (2.88 g) was refluxed with 3-methylpyridine (0.93 g) in benzene (15 ml) for 7 h. The product was chromatographed and elution of a yellow-brown band with ether gave 1,2-*dihydro*-9-*methyl*-4-*phenyl*-9aH-*quinolizin*-2-*one* (7) (392 mg, 17%), orange-red plates (from methanol), m.p. 174—175 °C (Found: C, 80.8; H, 6.5; N, 6.1. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.4; N, 5.9%); $\nu_{max.}$ 1 660, 1 630, 1 605, 1 578, 1 534, 1 491, 1 448, 1 429, and 1 404 cm^{-1}; $\lambda_{max.}$ (M) 213 (12 400), 269 (27 600), and 401 (12 700); (A) 215 (24 100), 267 (23 900), 285infl. (20 800), and 427 nm (5 800); *m/e* 237 (M^+, 43%), 236 (20), 209 (34), 208 (100), and 102 (27); *m** 184 (236→208).

(iv) *With quinoline*. 1-Phenylbut-1-yn-3-one (2.88 g) was refluxed with quinoline (2.58 g) for 2 h. Chromatography of the residue and elution of a yellow band with 50% ether–chloroform gave 3,4-*dihydro*-1-*phenyl*-4aH-*benzo*[c]-*quinolizin*-3-*one* (8) (308 mg, 5.6%), yellow needles (from methanol–chloroform), m.p. 157—160 °C (Found: C, 82.9; H, 5.5; N, 5.3. $C_{19}H_{15}NO$ requires C, 83.5; H, 5.5; N, 5.1%); $\nu_{max.}$ 1 679, 1 658infl., 1 651, 1 600, 1 590, 1 564, 1 550, 1 545infl., 1 489, 1 449, and 1 408 cm^{-1}; $\lambda_{max.}$ (M) 210 (ε 25 200), 229 (32 300), 287 (20 200), 343 (4 100) and 394 nm (4 500); *m/e* 273 (M^+, 48%), 244 (100), 129 (20), and 115 (25).

(v) *With benzimidazole*. 1-Phenylbut-1-yn-3-one (2.88 g) was refluxed with benzimidazole (2.36 g) in benzene (10 ml) for 28 h. On chromatography the first fraction gave (*Z*)-1-(3-*oxo*-1-*phenylbut*-1-*enyl*)*benzimidazole* (9), white crystals (from petrol–toluene), m.p. 79.5—81.5 °C (Found: C, 77.7; H, 5.4; N, 10.5. $C_{17}H_{14}N_2O$ requires C, 77.8; H, 5.4; N, 10.7%); $\nu_{max.}$ 1 693, 1 687infl., 1 605, 1 593, 1 582, 1 571, 1 489, 1 450, 1 445, and 1 418 cm^{-1}; $\lambda_{max.}$ (M) 215 (ε 19 100), 255infl. (14 700), 267 (15 200), and 303 (11 300); (A) 214 (18 100), 263 (15 400), 268 (15 300), and 274 nm infl. (14 300). Careful repeated chromatography of subsequent fractions gave (*E*)-1-(3-*oxo*-1-*phenylbut*-1-*enyl*)*benzimidazole* (10), white needles (from petrol–toluene), m.p. 115.5—117.5 °C (Found: C, 78.0; H, 5.4; N, 10.5. $C_{17}H_{14}N_2O$ requires C, 77.8; H, 5.4; N, 10.7%); $\nu_{max.}$ 1 665, 1 624, 1 488, 1 453, and 1 449 cm^{-1}; $\lambda_{max.}$ (M) 211 (ε 26 800), 228infl. (9 000), 254 (11 300), 274 (17 100), 290infl. (13 100); (A) 209 (11 900), 224 (9 700), 270 (15 700), 277 (15 700), and 287 nm infl. (14 100).

(vi) *With imidazole*. 1-Phenylbut-1-yn-3-one (2.88 g) was refluxed with imidazole (1.36 g) in toluene (10 ml) for 7 h. The product was distilled to give a pale yellow oil, b.p. 132—136 °C at 0.18 mmHg, which on trituration gave a sticky solid containing equal amounts of the *cis* and *trans* isomers (1.79 g, 42%). Recrystallisation from ether–acetonitrile gave 1-(3-*oxo*-1-*phenylbut*-1-*enyl*)*imidazole*, pale yellow needles, m.p. 77.5—79 °C (Found: C, 73.7; H, 5.7; N, 13.0. $C_{13}H_{12}N_2O$ requires C, 73.5; H, 5.7; N, 13.2%); $\nu_{max.}$ 1 683, 1 600infl., 1 589, 1 570, 1 515, 1 473, 1 462, and 1 446 cm^{-1}; $\lambda_{max.}$ (M) 209 (ε 14 700), 228infl. (8 800), 277 (13 800); (A) 209 (14 900), 225infl. (10 600), and 257 nm (8 100); τ ($CDCl_3$) 2.50—2.85 (2-H and ArH), 2.97 and 3.04 (d) (4-, 5-H, *J* 1.8 Hz), 3.70 (vinyl H, s), 3.70, and 8.06 (COMe, s). 1-Methyl- and 1,2-dimethylimidazole under similar conditions only gave tars.

(vii) *With* 1-*alkylbenzimidazoles*. An equimolar mixture of the 1-alkylbenzimidazole and 1-phenylbut-1-yn-3-one was refluxed in toluene to give (14)—(16). (14), 1,3-*dimethyl*-5-*phenyl*-1,6-*benzodiazocin*-2(1H)-*one* (Found: C, 78.0; H, 6.0; N, 10.3. $C_{18}H_6N_2O$ requires C, 78.2; H, 5.8; N, 10.1%); $\nu_{max.}$ 1 662, 1 658infl., 1 642infl., 1 635, 1 609, 1 595, 1 578, 1 482, and 1 429 cm^{-1}; $\lambda_{max.}$ (M) 257.5 (ε 17 200) and 323 (2 300); (A) 246 (4 400) and 305 nm (8 400); *m/e* 276 (M^+, 24%), 247 (12), 207 (8), 200 (15), 199 (100), and 171 (8); *m** 147 (188→171) and 143.5 (276→199). Iodine (5 g) in aqueous (50 ml) potassium iodide (10 g) was added dropwise with vigorous shaking and warming to a solution of (14) (70 mg) in water (4 ml) containing sodium hydroxide (0.1 g) and the minimum tetrahydrofuran until the iodine colour was no longer discharged. Dilution with an equal volume of water precipitated (14) (44 mg) and no iodoform could be detected. (15), 1-*ethyl*-3-*methyl*-5-*phenyl*-1,6-*benzodiazocin*-2(1H)-*one* (Found: C, 78.6; H, 6.3; N, 9.6.

Product	Reflux time (days)	M.p. (°C)	Appearance	Yield
(14) [a,d]	8	161.5—162	Cream prisms	0.50 g (9.3%)
(15) [b,d]	5	218.5—219.5	Colourless cubes	0.53 g (7.4%)
(16) [c,d]	3	150.5—152	Colourless plates	0.32 g (7.6%)

[a] Eluted with toluene from an alumina column. [b] Crystallised from reaction mixture at 0° C. [c] Eluted with toluene–chloroform (50 : 50) from an alumina column. [d] Crystals from methanol after decolourisation with animal charcoal.

$C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.3; N, 9.7%); $\nu_{max.}$ 1 661, 1 636, 1 608, 1 591, 1 578, 1 487, 1 430, and 1 420 cm^{-1}; $\lambda_{max.}$ (M) 258 (ε 18 300) and 327 (2 500); (A) 244 (5 200) and 306.5 nm (9 000); *m/e* 290 (M^+, 28%), 261 (10), 214 (17), 213 (100), 129 (11), and 77 (18); *m**, 160.8 (213→185), 156.5, (290→213), and 133.5 (185→157). (16), *1-benzyl-3-methyl-5-phenyl-1,6-benzodiazocin-2(1H)-one* (Found: C, 81.6; H, 5.7; N, 7.8. $C_{24}H_{20}N_2O$ requires C, 81.8; H, 5.7; N, 7.9%); $\nu_{max.}$ 1 660, 1 653infl., 1 630, 1 618infl. 1 606, 1 598infl., 1 572, 1 482, and 1 403 cm^{-1}; $\lambda_{max.}$ (M) 258.5 (ε 17 100) and 306infl. (4 000); (A) 253 (7 300) and 306 nm (9 000); *m/e* 352 (M^+, 32), 275 (40), 261 (27), 91 (100), and 77 (11); *m** 215 (352→275), 208 (261→233), 46.6 (91→65), and 30.1 (91→52).

Reactions of 2-Substituted Pyridines with Dimethyl Acetylenedicarboxylate (DMAD).—1-(2-Pyridyl)butan-2-one was prepared [29] from 2-methylpyridine, phenyl-lithium, and propiononitrile in 40.7% yield (b.p. 110—113 °C at 27 mmHg) (lit.,[29] 115 °C at 10 mmHg, 80%). 2-(Acetoxymethyl)-pyridine and 2-(benzoyloxymethyl)pyridine were prepared by treating 2-pyridylcarbinol with sodium hydride in benzene at 0°, followed by the appropriate acid chloride. 2-(Acetoxymethyl)pyridine distilled as a colourless liquid (9.44 g, 31.2%) (b.p. 110—111 °C at 28 mmHg) (lit.,[30] b.p. 106—108 °C at 2 mmHg) and 2-(benzoyloxymethyl)-pyridine as a pale yellow-green liquid (32.0 g, 74.5%) (b.p. 110—114 °C at 0.15 mmHg) (lit.,[30] b.p. 124—125 °C at 1.2 mmHg).

(i) *1-(2-Pyridyl)butan-2-one.* (*a*) 1-(2-Pyridyl)butan-2-one (8.97 g) and DMAD (17.10 g) were mixed in ether (100 ml). After 11 days at room temperature trituration with methanol precipitated *tetramethyl 4,5-dihydro-3-methylcyclopenta*[a]*quinolizine-1,2,4,5-tetracarboxylate* (20) (3.31 g, 13.2%), yellow plates (from methanol), m.p. 218—221 °C (Found: C, 60.9; H, 5.3; N, 3.2. $C_{21}H_{21}NO_4$ requires C, 60.7; H, 5.1; N, 3.4%); $\nu_{max.}$ 1 682, 1 630, 1 552, 1 530infl., 1 521infl., 1 516, and 1 410 cm^{-1}; $\lambda_{max.}$ (M) 227.5infl. (ε 10 300), 268 (11 300), 347 (8 000), and 449 (17 200); (A) 241 (6 900), 254infl. (5 000), 296 (3 000), 373 (15 000), and 449 nm (1 000); *m/e* 415 (M^+, 63%), 385 (9), 384 (38), 383 (20), 357 (24), 356 (100), 324 (11), 298 (11), 297 (46), 296 (8), 267 (7), 266 (36), 265 (23), 250 (10), 238 (9), 236 (6), 208 (11), 207 (23), 180 (25), 179 (45), 178 (23), 167 (7), 152 (16), and 59 (24); *m** 354 (415→383), 305.5 (415→356), 274 (383→324), and 155 (297→207). On column chromatography of the filtrate from (20) a red band was eluted with chloroform–toluene (70 : 30) which was re-chromatographed. Elution with toluene–chloroform (50 : 50) gave *trimethyl 1-propionyl-2-(methyloxycarbonylmethyl)-2H-quinolizine-2,3,4-tricarboxylate* (26) (42 mg, 0.16%) red platelets (from methanol–chloroform), m.p. 160—161.5 °C (Found: C, 58.2; H, 5.4; N, 3.2. $C_{21}N_{23}NO_9$ requires C, 58.2; H, 5.4; N, 3.2%); $\nu_{max.}$ 1 745, 1 732, 1 711, 1 624, 1 516, 1 437, and 1 425 cm^{-1}; $\lambda_{max.}$ (M) 212.5 (ε 17 300), 273 (14 000), 323 (6 000), and 470 (4 800); (A) 212 (13 800), 275 (8 700); *m/e* 433 (M^+, 8%), 377 (16), 376 (22), 375 (24), 374 (100), 360 (37), 345 (23), 344 (26), 342 (18), 319 (12), 318 (61), 317 (33), 316 (52), 286 (38), 284 (13), 258 (11), and 226 (17); *m** 316 (374→344), 291 (344→316), 270.5 (374→318), and 257 (318→286).

The 4,5-dihydrocyclopenta[*a*]quinolizine (20) (100 mg) was dissolved in chloroform (25 ml) and refluxed with *N*-bromosuccinimide (47 mg). After washing with water (2 × 20 ml) and drying evaporation gave a thick oil (see Table for ^1H n.m.r. spectrum).

Refluxing together (20) (100 mg) and 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (57 mg) in dioxan (20 ml) for 24 h, gave an oil whose ^1H n.m.r. spectrum was identical to that obtained in the previous experiment.

(*b*) 1-(2-Pyridyl)butan-2-one (2.50 g) and DMAD (4.75 g) were refluxed in toluene (30 ml) for 4 days and the solvent removed. Trituration of the residue with methanol gave tetramethyl 4,5-dihydro-3-methylcyclopenta[*a*]quinolizine-1,2,4,5-tetracarboxylate (20) (482 mg, 6.6%). The filtrate, on chromatography and elution with toluene, gave *dimethyl 1-propionylindolizine-2,3-dicarboxylate* (29) (56 mg, 1.2%) colourless prisms (from methanol), m.p. 118—120 °C (Found: C, 61.7; H, 5.4; N, 5.0. $C_{15}H_{15}NO_{15}$ requires C, 62.3; H, 5.2; N, 4.8%); $\nu_{max.}$ ($CHCl_3$ solution) 1 740, 1 696, and 1 660 cm^{-1}; $\lambda_{max.}$ [(M) and (A)] 225 (ε 22 400), 248 (36 700), 279infl. (10 000), 286 (12 500), 319.5infl. (22 600), 332 (25 200), and 347 infl. nm (15 200); *m/e* 291 (7%), 290 (6), 289 (M^+, 32), 261 (22), 260 (100), 258 (13), 202 (8), 143 (11), 116 (7), 115 (9), and 89 (7); *m** 234 (289→260), 204.2 (260→230), 177.5 (230→202).

(*ii*) *With 2-acetoxymethylpyridine.* 2-Acetoxymethyl-pyridine (1.64 g) and DMAD (3.12 g) were mixed in ether (15 ml) at 0 °C and left for 5 days. On evaporation and chromatography a red band, eluted with chloroform, gave *tetramethyl 1-acetoxy-4,5-dihydropyrido*[1,2-a]*azepine-2,3,-4,5-tetracarboxylate* (33) (132 mg, 2.8%), scarlet plates (from methanol–chloroform), m.p. 138—140 °C (decomp.) (Found: C, 55.4; H, 5.0; N, 3.1. $C_{20}H_{21}NO_{10}$ requires C, 55.2; H, 4.9; N, 3.2%); $\nu_{max.}$ 1 764, 1 744, 1 731, 1 720infl., 1 677, 1 662infl., 1 631, 1 573, 1 530, 1 496, and 1 431 cm^{-1}; $\lambda_{max.}$ (M) 254 (ε 8 700), 384infl. (11 300), 394 (12 700), 489 (15 700); (A) 213 (12 300) and 301 nm (8 900); *m/e* 435 (M^+, 6%), 404 (6), 393 (7), 392 (7), 376 (21), 375 (17), 362 (13), 361 (28), 345 (31), 344 (24), 343 (47), 334 (27), 333 (8), 330 (30), 329 (21), 314 (22), 313 (40), 312 (100), 302 (55), 301 (20), 274 (33), 254 (22), and 217 (21); *m** 324.5 (435→376), 313 (376—343), 302 (361→330), 284 (393→334), 274 (333→302), and 270 (435→343).

(iii) *With 2-benzoyloxymethylpyridine.* 2-Benzoyloxy-methylpyridine (9 g) and DMAD (12 g) were mixed in ether (50 ml) at 0 °C and left for 5 days. On chromatography a red band eluted with chloroform–toluene (25 : 75) gave *tetramethyl 1-benzoyloxy-4,5-dihydropyrido*[1,2-a]*azepine-2,-3,4,5-tetracarboxylate* (34) (877 mg, 4.2%), red crystals (from methanol), m.p. 121—125 °C (decomp.) (Found: C, 59.8; H, 4.9; N, 2.8. $C_{25}H_{23}NO_{10}$ requires C, 60.3; H, 4.7; N, 2.8%); $\nu_{max.}$ 1 800infl., 1 749infl., 1 730, 1 690, 1 632, 1 600, 1 579, 1 531, 1 510infl., 1 495infl., 1 472, and 1 462 cm^{-1}; $\lambda_{max.}$ (M) 235 (ε 25 400), 370infl. (11 300), 396 (12 800), and 490 (15 600); (A) 249 (21 800) and 300 nm (9 900); *m/e* 123 (10%), 122 (81), 106 (10), 105 (100), 78 (13), 77 (81), 76 (8), 74 (10), 52 (8), 51 (40), and 50 (24).

Thermal Decomposition of (33) *and* (34).—Tetramethyl 1-acetoxy-4,5-dihydropyrido[1,2-*a*]azepine-2,3,4,5-tetra-carboxylate (33) (70 mg) was refluxed in benzene (10 ml) for 19 h. Evaporation of benzene and trituration with methanol gave *tetramethyl 1-(1,2-dihydro-2-pyridinylidene)-cyclopenta-2,4-diene-2,3,4,5-tetracarboxylate* (36) (42 mg, 70%) pale yellow needles (from methanol–ether), m.p. 150 °C, resolidifying and melting 225—235° (decomp.) (Found: C, 57.9; H, 4.7; N, 3.7. $C_{18}H_{27}NO_8$ requires C, 57.6; H, 4.6; N, 3.7%); $\nu_{max.}$ 3 250, 3 170, 1 725infl., 1 698, 1 682infl., 1 626, 1 610, 1 540, and 1 456 cm^{-1}; $\lambda_{max.}$ (M) 225 (ε 21 800), 267 (35 800), and 306 (17 800); (A) 213 (22 500), 261 (35 000), and 389 nm (6 500); *m/e* 375 (M^+,

3%), 344 (11), 343 (50), 313 (19), 312 (100), 282 (8), 254 (8). 185 (8), 141.5 (5), and 141 (5). Similar treatment of (34) also gave (35) (53.4%).

(iv) *With 2-(methoxymethyl)pyridine.* 2-Methoxymethylpyridine (32) was obtained [1.07 g, b.p. 70—73 °C at 20 mmHg (lit.,[31] 45—55 °C at 4 mmHg)] by adding methyl iodide (7.1 g) in ether to a mixture of 2-pyridylmethanol (5.45 g) in ether (25 ml) which had been stirred with sodium hydride (50% oil dispersion, 3 g) for 15 min. After refluxing for 15 h, filtration and distillation gave (33). DMAD (1.23 ml) was added to (33) (1.23 g) in ether (25 ml) at −60 °C and the mixture allowed to warm to 0 °C. After 2 weeks the *azepine* (35), pink crystals (6 mg) (from methanol–ether), m.p. 139—145 °C, was obtained (Found: C, 56.2; H, 5.2; N, 3.2. $C_{19}H_{21}NO_9$ requires C, 56.0; H, 5.2; N, 3.5%); $\nu_{max.}$ 1 751, 1 733, 1 668, 1 632, 1 578, 1 488, and 1 442 cm^{-1}; $\lambda_{max.}$ (M) 208 (ε 9 500), 236 (7 300), 252 (7 900), 405 (11 700), and 505 (14 300); (A) 207 (11 200), 255 (5 700), and 321 nm (5 900); *m/e* 407 (M^+, 41), 393 (24), 392 (100), 376 (31), 361 (22), 360 (96), 348 (53), 332 (37), 316 (25), 300 (18), 274 (38), and 248 (24); *m** 331 (392→ 360).

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