Addition Reactions of Heterocyclic Compounds. Part LXI.[1] Reactions of Electrophilic Acetylenes with Conjugated Cyclic Enamines

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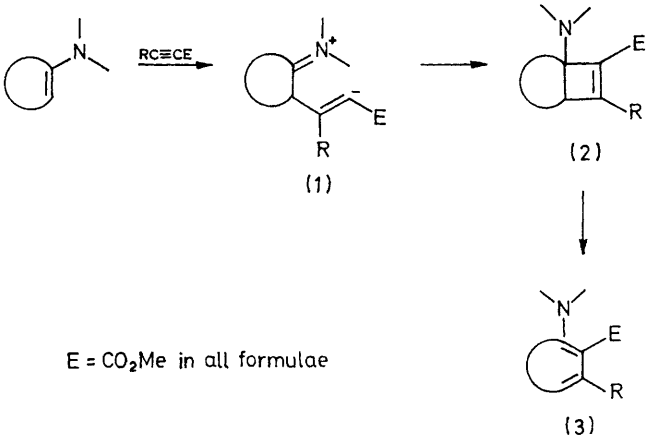
[1-Alkylpyridin-4(1*H*)-ylidene] acetates and related compounds react at the exocyclic double bond with electrophilic acetylenes to give 1 : 1 and 1 : 2 adducts by simple Michael addition followed by proton shift. With tetracyanoethylene a related product was isolated and also a compound in which the ester group had been lost. Methyl [1-alkylpyridin-2(1*H*)-ylidene] acetates give analogous products with methyl propiolate, but-3-yn-2-one, and 4-phenylbut-3-yn-2-one.

ALICYCLIC enamines react with electrophilic acetylenes to give zwitterions (1) which initially ring-close to afford bicyclic compounds (2); these can then undergo ring-opening to give monocyclic compounds (3), depending on the substituents and the size of the ring.[2-5] Similar behaviour is found with indole,[6] 3-dialkylaminoindoles,[7] and 1,2-dihydro-[8] and 1,4-dihydro-pyridines.[9] We have



now examined reactions of some electrophilic acetylenes with dihydropyridines possessing an exocyclic double bond.

Compounds (4)—(7) were obtained by the action of base on the appropriate quaternised pyridine.[10] Compounds (4)—(6) reacted with dimethyl acetylenedicarboxylate in chloroform to give the bright red dihydropyridines (8)—(10). With diethyl acetylenedicarboxylate compound (5) gave the dihydropyridine (11) and a closely similar 1 : 2 adduct which has been assigned structure (12). The n.m.r. spectra of compounds (8)—(12) showed the ring proton signals at similar positions to those of (4)—(6) but the vinyl proton resonance had been replaced by a signal at the correct position for a fumarate chain.[11] Models suggest that the fumarate unit is unlikely to be coplanar with the rest of the molecule, and this is supported by the spectra of compounds (8) and (9) in trifluoroacetic acid which show that protonation occurs at the 2'-position.

The dihydropyridines (4)—(6) with methyl propiolate gave the 1 : 1 adducts (13)—(15). The n.m.r. spectra of these contained AB quartets (J 15 Hz) and low field A_2B_2 systems showing that the ester and the *trans*-acrylate group have essentially the same deshielding effect; resonance contributions by charged forms such as (22) (*cf.* ref. 12) could make the 4,2'-double bond less rigid than normal. Minor products from compounds (5) and (6) were (16) and (24). The structure (24) was deduced by comparison of spectra with those of other indolizines.[13] A route for this merely requires a proton shift in (6) to form the ylide (23),[14] followed by Michael addition and cyclisation. The dihydropyridine (4) with but-3-yn-2-one and its 4-phenyl derivative gave compounds (17) and (18), respectively.

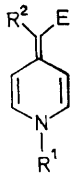
Scheme 1 shows two routes to these adducts. Initial electrophilic attack by the acetylene at the 4-substituent of the dihydropyridine [*e.g.* (4)] would give a zwitterion, which could either undergo a proton shift, or cyclise to a cyclobutene (25) and ring-open as shown. The evidence favours the former route.

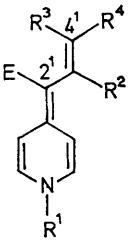
Hydrolysis and decarboxylation of the adduct (17) gave the pyridine (26), the structure of which follows from spectral comparisons with (27).[13] The dihydropyridine (7) with dimethyl acetylenedicarboxylate gave only tar; migration of a methyl group to a negative centre is not expected, and cyclobutene formation would not be affected.

Tetracyanoethylene with the dihydropyridine (4) gave mainly compounds (21) and (29), hydrogen cyanide being eliminated as in many reactions of this olefin, and a trace of the diester (28), identified from its spectra and comparison (u.v.) with the corresponding diethyl ester.[15] The *N*-methyl n.m.r. signals for compounds (21) and (29) are at low field, indicating the presence of considerable positive charge on the rings, but although the u.v.

[1] Part LX, R. M. Acheson and J. M. Woollard, preceding paper.
[2] G. A. Berchtold and G. F. Uhlig, *J. Org. Chem.*, 1963, **28**, 1454.
[3] C. F. Huebner, L. Dorfman, M. M. Robison, E. Donoghue, W. G. Pierson, and P. Strachan, *J. Org. Chem.*, 1963, **28**, 3124.
[4] K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, 1964, **29**, 818.
[5] A. J. Birch and E. G. Hutchinson, *J. Chem. Soc.* (*C*), 1971, 3671.
[6] R. M. Acheson, J. N. Bridson, and T. S. Cameron, *J. Chem. Soc.* (*C*), 1972, 968.
[7] M.-S. Lin and V. Snieckhus, *J. Org. Chem.*, 1971, **36**, 645.
[8] R. M. Acheson and G. Paglietti, *J.C.S. Chem. Comm.*, 1973, 665.
[9] R. M. Acheson, N. D. Wright, and P. A. Tasker, *J.C.S. Perkin I*, 1972, 2918; R. M. Acheson and N. D. Wright, *Chem. Comm.*, 1971, 1421.
[10] R. A. Jones and A. R. Katritzky, *Austral. J. Chem.*, 1964, **17**, 455.
[11] N.m.r. Spectra Catalog, Varian Associates, Palo Alto, 1962.
[12] G. H. Crabtree and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1967, **87**, 2908.
[13] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1969, 2311.
[14] C. A. Henrick, E. Ritchie, and W. C. Taylor, *Austral. J. Chem.*, 1967, **20**, 2467.
[15] G. V. Boyd and A. D. Ezekiel, *J. Chem. Soc.* (*C*), 1967, 1866.

spectrum of (21) resembled those of (13) and analogous compounds, the u.v. spectrum of (29) was quite different. The ring protons of (29) gave rise to an A_2B_2 system in the n.m.r. spectrum, indicating that the molecule might be

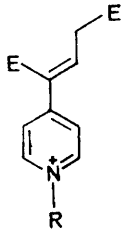




	R^1	R^2
(4)	Me	H
(5)	CH_2Ph	H
(6)	CH_2E	H
(7)	Me	Me

	R^1	R^2	R^3	R^4
(8)	Me	E	E	H
(9)	CH_2Ph	E	E	H
(10)	CH_2E	E	E	H
(11)	CH_2Ph	CO_2Et	CO_2Et	H
(12)	CH_2Ph	CO_2Et	CO_2Et	*trans*-C(CO_2Et):CH CO_2Et
(13)	Me	H	H	E
(14)	CH_2Ph	H	H	E
(15)	CH_2E	H	H	E
(16)	CH_2Ph	H	*trans*-CH:CHE	E
(17)	Me	H	H	Ac
(18)	Me	Ph	H	Ac
(19)	Me	H	*trans*-CE:CHE	E
(20)	Me	H	*trans*-CE:CHE	Ac
(21)	Me	CN	CN	CN

symmetrical. The i.r. spectrum showed one strong C≡N absorption, at 2198 cm^{-1}, in contrast to (21) which showed



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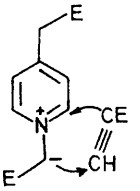

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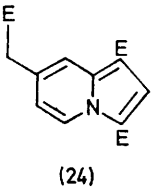


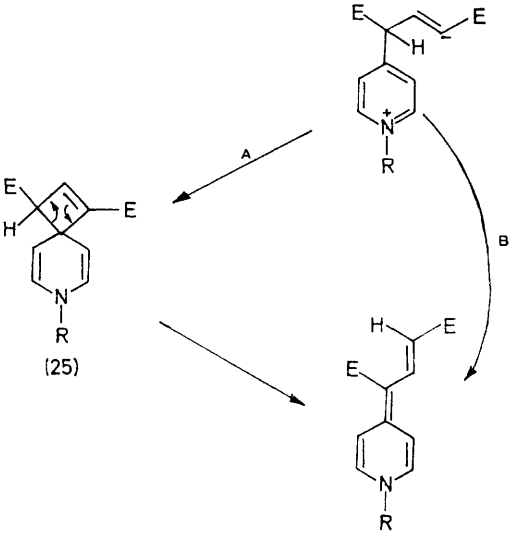
(24)

several, and the long-wavelength position is consistent with some double bond character in the carbon–nitrogen links. Thus the zwitterion structure gives a better representation of the compound than uncharged structures; moreover the cyano-group is known to stabilise negative charge.[16]

Compound (8), in which the fumarate side-chain can hardly be coplanar with the ring, did not react with methyl propiolate. The dihydropyridines (13) and (17), in which coplanarity with the ring and maximum resonance interaction with the ring are sterically possible, both reacted with dimethyl acetylenedicarboxylate. Compound (13) gave the dihydropyridine (19), with some pentamethyl benzenepentacarboxylate, *via* Scheme 2, and compound (17) gave the dihydropyridine (20).

[16] C. Leonte and I. Zugravescu, *Tetrahedron Letters*, 1972, 2029.
[17] B. R. Baker and F. J. McEvoy, *J. Org. Chem.*, 1955, **20**, 118.

Compounds (32)—(35) were synthesised as above,[10] and with the appropriate acetylene gave the deep red dihydropyridines (36)—(42); in these cases the 1 : 2 adducts were formed rather readily. These reactions parallel the formation [17] of (31) from (30) with phenyl isocyanate. A second product in the reaction of 4-phenylbut-3-yn-2-one with (32) was the furan (43), in which a major contribution by the illustrated charged structure accounts for the low-field positions of the



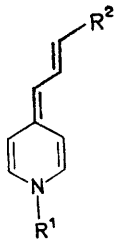
(25)

Scheme 1

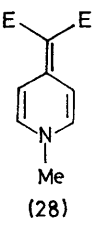
n.m.r. signals due to the 6-proton and *N*-methyl group. The base peak in the mass spectrum was at $M - 99$,

corresponding to loss of $C_4H_3O_3$, a fragment most easily derived from the five-membered ring.

We hoped that the imine (44) would give compounds analogous to (8), but with methyl propiolate the only



	R^1	R^2
(26)	Me	Ac
(27)	*trans*-CH:CHE	E



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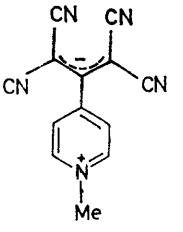
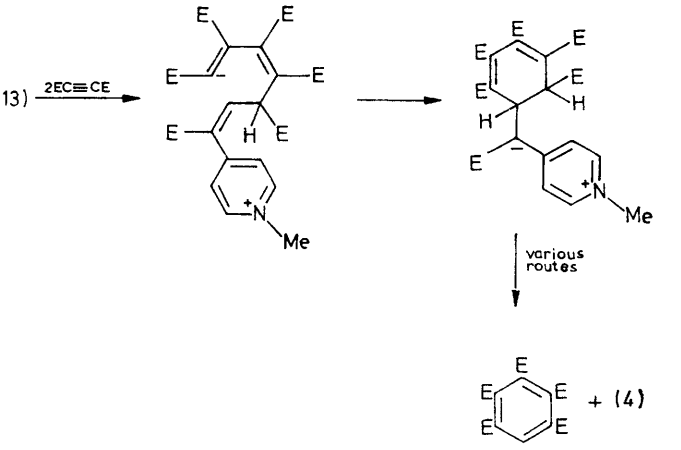


(29)

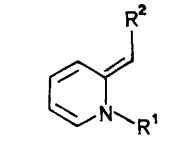
product was the azaheptadienedioate (45). The required deamination of the pyridine has precedent in the acid-catalysed deamination of 9-diacetylaminoacridine.[18]

In no experiment did we find any evidence for attack

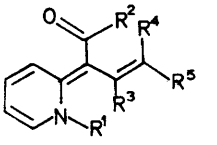


SCHEME 2

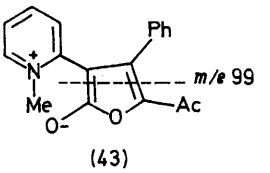
available as supplementary publication No. SUP 21254 (11 pp.; 1 microfiche),* which also gives details of the i.r. and mass spectra. Representative u.v. and n.m.r. spectra only are listed in Tables 1 and 2; these types of spectra for all the other new compounds are available in the Supplementary Publication.



	R^1	R^2
(30)	CH_2Ph	H
(31)	CH_2Ph	CO·NHPh
(32)	Me	E
(33)	CH_2Ph	E
(34)	Me	CO_2Et
(35)	Me	COEt



	R^1	R^2	R^3	R^4	R^5
(36)	Me	OMe	H	*trans*-CH:CHE	E
(37)	CH_2Ph	OMe	H	*trans*-CH:CHE	E
(38)	Me	Et	H	*trans*-CH:CHE	E
(39)	Me	Et	H_a	H_b	E
(40)	Me	OMe	H	*trans*-CH:CHAc	Ac
(41)	Me	OMe	H_a	H_b	Ac
(42)	Me	OMe	Ph	H	Ac



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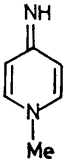

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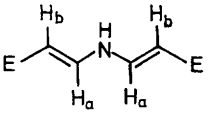

(45)

at a double bond other than the exocyclic one, nor for formation of cyclobutenes, even as intermediates.

EXPERIMENTAL

The instruments and procedures have been described in earlier papers in the series. All analyses for new compounds were within accepted limits for C, H, and N and are

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

But-3-yn-2-one [19] and 4-phenylbut-3-yn-2-one [20] were prepared as described.

[18] A. M. Grigorovsky, *Compt. rend. Acad. Sci. U.S.S.R.*, 1946, **53**, 229.

[19] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

[20] D. Nightingale and F. Wadsworth, *J. Amer. Chem. Soc.*, 1945, **67**, 416.

General Procedure for the Preparation of 2- and 4-Methylene-substituted Dihydropyridines.—The appropriate 2- or 4-methylpyridine was stirred with an equimolar quantity of an alkyl halide in ether, with gentle warming if necessary. After 6 h the salt, which sometimes formed as an oil, was dissolved in water, and an equimolar amount of 2N-sodium hydroxide was added. The product was extracted with chloroform and the extract dried ($MgSO_4$), filtered, and evaporated to give the pyridine, which was then recrystallised. The results are summarised in Table 3.

General Procedure for Reactions between 2- and 4-Methylene-substituted Dihydropyridines and Acetylenes.—The acetylene

TABLE 1

N.m.r. spectra [a] (60 MHz; τ values; J in Hz) for solutions in deuteriochloroform with tetramethylsilane as internal standard

Compound	Proton resonances	Ester Me
(4)	2,6-H_2, 3·3—3·5m; 3-H, 2·32q; 5-H, 3·97; $J_{2,3} = J_{5,6} = 7·7$; $J_{2,6} = J_{3,5}$ 2·5; vinyl H, 5·26; NMe, 6·62	6·40
(8)	2,6-H_2, 3·25br; [b] 3-H, 1·96br,d; 5-H, 4·00br,d; $J_{2,3} = J_{5,6} = 7·5$; 4′-H, 3·34; NMe, 6·60	6·33, 6·42, 6·50
(8) [c]	2,6-H_2, 1·33d; 3,5-H_2, 1·69; $J_{2,3}$ 6·7; 1-Me, 5·58; 2′-H, 3·53; 4′-H, 2·70	6·08, 6·10, 6·12
(11)	2,6-H_2, 3·05,[b] J 8·4; 3-H, 1·97br,d; 5-H, 3·98br,d; vinyl H, 3·36; N·CH_2, 5·25; ArH_5, 2·82;[d] $(O·CH_2)_2$, 5·88q, 6·08q; $(CH_3·CH_2)_2$, 8·83t, 8·94t, J_{Et} 7·2	6·54
(12)	ArH_5, 2,6-H_2, 2·55—3·2m; 3-H, 1·9br,d; 5-H, 3·95d; $J_{2,3} = J_{3,5} = 8$; vinyl H, 3·32; N·CH_2, 5·29; $(OCH_2)_4$, 5·85br,q; $(OCH_2·CH_3)_4$, 8·65—9·0m	6·48
(13)	2,6-H_2, 3·04d;[e] 3,5-H_2, 2·53br,d;[e] $J_{2,3}$ 7·8; 3′-H, 2·16d; 4′-H, 3·92, J 15	6·29, 6·32, 6·46 [f]
(17)	2,6-H_2, 2·91d;[e] 3,5-H_2, 2·49d;[e] $J_{2,3}$ 8·0; 3′-H, 2·15d; 4′-H, 3·53d, J 15·1; Ac, 7·78	6·28, 6·38 [f]
(17) [c]	2,6-H_2, 1·25;[g] 3,5-H_2, 1·95,[g] J 7; NMe_2, 5·51, 5·56; Ac, 7·55, 7·68; set (a): 3′-H, 2·80t; 4′-H_2, 5·82d, J 6·8; set (b): 3′-H, 2·28t; 4′-H_2, 6·47d, J 7·4	6·04, 6·08
(19)	ring-H_4, 2·8—3·2m; 3′-H, 2·15; 6′-H, 3·51	6·32, 6·38, 6·42, 6·43, 6·46 [f]
(19) [c]	2,6-H_2, 1·27d; 3,5-H_2, 1·88d; $J_{2,3}$ 6·6; 3′-H, 2·55d; 4′-H, 5·11d,[h] J 10·5; 6′-H, 2·69; NMe, 5·55	
(21) [i]	2,6-H_2, 1·35d; 3,5-H_2, 2·11d; $J_{2,3}$ 6·9; NMe, 5·82	6·38
(24)	2-H, 2·12; 5-H, 0·62q; 6-H, 3·13q; 7-CH_2, 6·34; 8-H, 1·84q; $J_{5,6}$ 7·2; $J_{5,8}$ 1·2; $J_{6,8}$ 2·0	6·15, 6·34
(26) [j]	5-H, 4·05br,d, J 8; 1′-H, 4·75d, J 13·2; 2′-H, 2·35q; 3′-H, 4·25d, J 14·4; Ac, 7·90; NMe, 6·70	
(28)	2,6-H_2, 3·07d; 3,5-H_2, 2·54d; $J_{2,3}$ 8·1; NMe, 6·47	6·29, 6·29
(29) [i]	2,6-H_2, 1·44d; 3,5-H_2, 2·31d; $J_{2,3}$ 6·8; NMe, 5·87	
(29) [c]	2,6-H_2, 1·65d; 3,5-H_2, 2·11d; $J_{2,3}$ 6·8; NMe, 5·76	
(32)	3-H, 1·62q; 4-H, 3·1m; 5-H, 4·09;[k] 6-H, 3·04d; $J_{3,4}$ 10·5; $J_{3,5}$ 1·5; $J_{4,5} = J_{5,6} = 6·6$; vinyl H, 5·63; NMe, 6·75	6·39
(38)	3-H, 2·44q; 4-H, 2·06t;[l] 5-H, 2·73m; 6-H, 1·77d; $J_{3,4}$ 8·4; $J_{3,5}$ 1·8; $J_{4,5}$ 7·8; $J_{5,6}$ 6·6; 3′-H, 1·82; 5′-H, *ca.* 3·0; 6′-H, 4·05d, J 15; NMe, 6·02; CO·CH_2, 7·26q; $CH_2·CH_3$, 8·83t, J_{Et} 7·2	6·45, 6·45
(38) [i]	3,5-H_2, 2·25—2·55m; 4-H, 1·85m; 6-H, 1·18d; $J_{5,6}$ 6; 3′-H, 2·02; 5′-H, 3·37d; 6-H, 4·30d; J 15; NMe, 6·12; CO·CH_2, 7·41q; $CH_2·CH_3$, 8·98t, J_{Et} 7·2	6·58, 6·58
(39)	3,4-H_2, 2·05m; 5-H, 2·79m; 6-H, 1·75br,d; $J_{5,6}$ 6; H_a, 1·88d; H_b, 5·25d, $J_{a,b}$ 14·7; NMe, 6·08;[e] CO·CH_2, 7·36q; $CH_2·CH_3$, 8·83t, J_{Et} 7·2	6·37 [e]
(39) [c]	3,5-H_2, 1·8—2·15m; 4-H, 1·35m; 6-H, 1·10d; $J_{5,6}$ 6; 3′-H, 2·12t; 2′-H_2, 6·58d, J 7·2; NMe, 5·78; CO·CH_2, 6·87q; $CH_2·CH_3$, 8·73t, J_{Et} 7·2	6·12
(43) [i,m]	3-H, 3·15d; 5-H, 2·22t; 5-H, 2·62m; 6-H, 1·36d; $J_{3,4} = J_{4,5} = 8·5$; $J_{5,6}$ 5·5; ArH_5, 2·66;[d] NMe, 5·79; Ac, 8·03	
(45) [i]	NH, −0·02br,t, J 11·4; 2 × H_a, 2·38q; 2 × H_b, 4·85d, $J_{a,b}$ 13·7	6·45, 6·45

[a] Many of the spectra include A_2B_2 systems, and the J values recorded are those measured from the spectra assuming a first-order interpretation. [b] Apparent doublet. [c] In trifluoroacetic acid. [d] Apparent singlet. [e] Assignments could be reversed. [f] Includes an *N*-methyl. [g] Apparent triplet. [h] Could be at 2′-position. [i] In [$^2H_6$]dimethyl sulphoxide. [j] As a mixture with (17). [k] Six lines. [l] With further splitting. [m] At 100 MHz.

TABLE 2

U.v. spectra

Compound	Solvent [a]	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$ in parentheses)
(5)	M	210 (2·54), 255infl (0·93), 368 (2·52), 420 (0·73)
	A	211 (2·55), 260infl (0·77)
(7)	M	207 (0·52), 224 (0·67), 258 (0·42), 264 (0·37), 379 (0·65)
	A	205 (0·41), 225 (0·66), 258 (0·48), 264 (0·41)
(8)	M	210 (1·59), 366 (2·25), 430 (0·61)
	A	215 (1·92), 255infl (1·47), 261 (0·55), 267infl (0·51)
(16)	M	212 (2·30), 250infl (0·92), 293 (1·90), 390 (1·13), 501 (2·57)
	A	212 (2·33), 245infl (1·26), 260infl (1·16), 290 (0·88)
(20)	M	235 (1·13), 337 (1·22), 469 (2·15)
	A	235 (1·10), 257infl (0·88), 266infl (0·77), 285infl (0·43), 375 (0·27)
(21)	M	220 (1·19), 269 (1·06), 354 (1·14), 488 (1·89)
	A	220 (1·02), 246 (1·14), 370infl (0·55), 433 (1·40)
(24)	M, A	225 (1·87), 243infl (3·03), 248 (3·76), 270infl (1·24), 277 (1·59), 320infl (1·63), 331 (1·70)
(28)	M	208 (0·74), 230 (0·66), 260 (0·51), 371 (3·42)
	A	206 (0·45), 226 (0·61), 261 (0·45), 266 (0·42)
(29)	M, A	235infl (0·72), 267infl (0·50), 320infl (0·52), 367infl (0·72), 394 (0·90), 414 (0·91), 489 (1·40), 560 (1·95)
(32)	M	210 (0·71), 255infl (0·18), 305 (1·69), 313 (1·94), 384 (0·73)
	A	209 (0·45), 265 (0·65)
(43)	M	258 (0·79), 353 (0·99), 436 (1·50)
	A	267 (0·80), 308 (0·78), 381 (1·34)
(45)	M	313 (1·22)
	A	313 (0·75)

[a] M, methanol; A, methanol acidified with 1 drop of 72% perchloric acid.

TABLE 3

Dihydropyridines

Compound	Cryst. solvent	M.p. (°C)	Appearance	Yield (%)
(4)	MeOH	111—112·5	Silvery parallelipipeds	60
(5)	MeOH–$CHCl_3$	159—160	Pale brown rods	74
(6)	Et_2O–MeOH	124—125·5	Silver plates	40
(7)	Et_2O–MeOH	107—110	Plates	67
(32)	Petroleum–PhMe	93—94	Yellow plates	80
(33)	MeOH	125—127	Yellow needles	79
(34) [a]	MeOH	50—52	Yellow	25
(35)	Et_2O–MeCN	67—69·5	Yellow needles	43

[a] Lit.,[10] m.p. 52—54°.

TABLE 4

Products of reactions with acetylenes

Compound	Crystallisation solvent	M.p. (°C)	Appearance	Yield (%)
(8)	MeOH–$CHCl_3$	176—180	Vermilion	63
(9) [a]	MeOH–$CHCl_3$	117—122 [b]	Cerise needles	57
(10)	MeOH–$CHCl_3$	153—156	Scarlet prisms	29
(11) [a]			Red gum	
(12) [a]			Crimson gum	30
(13)	MeOH–$CHCl_3$	184—185·5	Yellow micro-needles	56 [c]
(14) [d]	MeOH–Et_2O	147—149·5	Red	
(15)	MeOH–$CHCl_3$	180·5—182·5	Yellow micro-needles	45
(16) [a,e]	MeOH–Et_2O	138—140	Red plates	
(17)	MeOH–Et_2O	166—168	Red	38 [c]
(18) [a]	MeOH–Et_2O	182—184	Orange-red rods	17
(19) [a]	*f*	60—65	Red	20
(20) [a]	*g*	136—141	Cerise	36
(21)	Me_2CO	241—243	Orange	*h*
(23) [i]	MeOH	118—123	Fluffy needles	3
(28) [i]	MeOH	163—165·5	Pale yellow rhombs	1
(29)	MeOH–Me_2CO	230—235	Intense violet microcrystals	*h*
(36) [a]	MeOH [i,j]	150—154	Crimson crystals	
		165·5—167·5	Cerise powder	29
(37) [a]	Et_2O–MeOH	130—133	Maroon	26
(38) [a]			Red gum	39
(39) [a]			Red gum	16
(40) [d]	*k*	162—168	Crimson powder	
(41) [a]			Carmine gum	
(42) [a]	*k*	145—150	Yellow micro-crystals	12
(43) [a]	MeOH	Sub. 240	Crimson	3
(45) [a,l]	MeOH	196—198	Needles	5

[a] Isolated after chromatography. [b] After three recrystallisations. [c] Includes more material obtained after chromatography of the residue. [d] After double chromatography of a part sample R_F(methanol) (14) 0·71, (16) 0·72. [e] Isolated by fractional crystallisation. [f] Decomposed to (8) on attempted recrystallisation. [g] Decomposed on attempted recrystallisation. [h] Isolated as a mixture of (21) and (29): partial separation achieved by hand. [i] From chromatography of the filtrate. [j] Recrystallisation gave two forms, separable by hand. [k] Could not be recrystallised. [l] Reaction solvent toluene.

(0·03 mol) was added at room temperature to the pyridine (0·015 mol) in chloroform (20 ml). The mixture rapidly darkened and became warm. After several days the solvent was evaporated off and the residue triturated with methanol; if this failed to give any solid, the residue was chromatographed. The results are summarised in Table 4.

Methyl 2-(4-*Pyridyl*)*propionate*.—Sodium hydride (50% dispersion in oil; 1·9 g) was first washed with dry petroleum and then added to methyl (4-pyridyl)acetate (4·87 g) in dry benzene (20 ml). The mixture was refluxed for 90 min, then cooled, and methyl iodide (4·6 g) in benzene (5 ml) was added before refluxing for a further 90 min. The solid was filtered off, and the filtrate distilled to give the ester (53%), b.p. 107—115° at 20 mmHg, $\nu_{max.}$ 1745, 1604, 1565, 1499, 1460, 1438, and 1419 cm^{-1}.

In a similar preparation using methyl (2-pyridyl)acetate, the n.m.r. spectrum of the oily product indicated that the methylation proceeded to the extent of only 50%.

Attempted Hydrolysis of the Dihydropyridine (17).—Compound (17) (120 mg) was dissolved in water (5 ml) containing potassium hydroxide (0·6 g) by boiling. After 2 h the deep red solution was extracted with chloroform (4 × 4 ml). The n.m.r. spectrum of the extracted material, a crimson gum, showed signals due to compound (17) and to 5-[1-methylpyridin-4(1*H*)-ylidene]pent-*trans*-3-en-2-one (26), in approximately equal amounts.

1-*Methylpyridin*-4(1H)-*imine* (49).—The imine, prepared as reported [21] by the action of concentrated aqueous potassium hydroxide on 4-amino-1-methylpyridinium iodide, and extraction into hot toluene, had m.p. *ca.* 130° (crude solid), $\nu_{max.}$ 3280br, 1673, 1665, 1545, and 1450 cm^{-1} [lit.,[22] $\nu_{max.}$ ($CHCl_3$) 1655 and 1542 cm^{-1}].

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[21] L. C. Anderson and N. V. Seegar, *J. Amer. Chem. Soc.*, 1945, **71**, 340.

[22] C. L. Angyal and R. L. Werner, *J. Chem. Soc.*, 1952, 2911.