Addition Reactions of Heterocyclic Compounds. Part LVII.[1] Reactions of Pyridines with Acetylenic Esters in the Presence of Carbanion Sources

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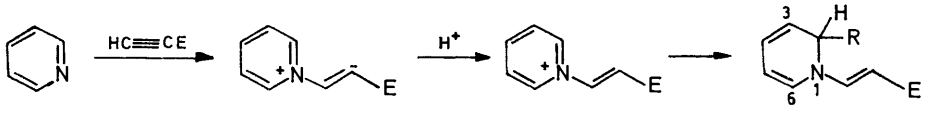
Pyridine, methylpyridines, isoquinoline, and acridine react with methyl propiolate and nitromethane to give mainly dihydro-*N*-*trans*-methoxycarbonylvinyl derivatives with a nitromethyl group usually *para* to the ring nitrogen atom. Replacing nitromethane by methyl acetoacetate or cyanoacetate, acetylacetone, or malononitrile, gives corresponding products. Acridine reacts with dimethyl acetylenedicarboxylate in nitromethane to give Diels and Alder's 'red adduct,' identified as tetramethyl pyrido[2,1-*e*]acridine-1,2,3,4-tetracarboxylate. The structures of the new compounds are deduced mainly from their n.m.r. spectra.

DIHYDROPYRIDINES [*e.g.* (3)] have been obtained from methyl propiolate and pyridines in ether,[2,3] the initially formed carbanion (1) abstracting a proton from a second mole of the acetylene to form the pyridinium cation (2) with subsequent combination of the counterions. In the presence of 1 mole of methanol, 2-methoxy-1,2-dihydropyridines [*e.g.* (7)] were formed similarly.[3] Further studies of the products obtained by adding acetylene-mono- and -di-carboxylic esters to pyridine in the presence of other proton donors are now reported.

Some pyridines, isoquinoline, and acridine reacted with methyl propiolate in the presence of nitromethane to give the 1,4-dihydropyridines (9)—(11), the 1,2-dihydroisoquinoline (25), and the acridan (38). Comparison of the n.m.r. spectra of (9)—(11) with that of (24),[4] and of (25) with that of (26)[5] showed that the acrylate protons were *trans* and confirmed the position of the substituents. The asymmetric C-1 of (25) gave rise to a typical ABX pattern for the neighbouring CH_2NO_2 protons, but such an effect was not observed with compound (10), presumably because the 3-methyl group had only a small effect on the magnetic environment. Accompanying compounds

[1] Part LVI, R. M. Acheson, G. Paglietti, and P. A. Tasker, *J.C.S. Perkin I*, 1974, 2496.
[2] A. Crabtree, A. W. Johnson, and J. C. Tebby, *J. Chem. Soc.*, 1961, 3497.
[3] R. M. Acheson and J. M. Woollard, *J. Chem. Soc.* (*C*), 1971, 3296.
[4] H. Albrecht and F. Kröhnke, *Annalen*, 1968, **717**, 96.
[5] R. M. Acheson and M. S. Verlander, *J. Chem. Soc.* (*C*), 1969, 2311.

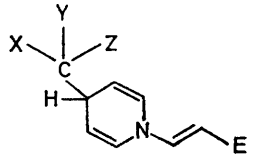
(9)—(11) were approximately equal amounts of the corresponding ethynyl adducts (3), (4), and (6), and the only isolable product from the reaction of 4-methylpyridine was compound (5).



(1) (2) (3) R = C≡CE; (4) 3-Me, R = C≡CE; (5) 4-Me, R = C≡CE; (6) 3,5-Me_2, R = C≡CE; (7) R = OMe; (8) 3,5-Me_2, R = CHE·Ac

E = CO_2Me

Quinoline gave a low yield of the pyrroloquinoline (31),[5] and a tentative route for the formation of this requires [6] the participation of an ion such as MeO^-;

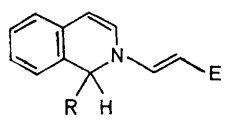


		X	Y	Z
(9)		H	H	NO_2
(10)	3-Me	H	H	NO_2
(11)	3,5-Me_2	H	H	NO_2
(12)		H	Me	NO_2
(13)	3-Me	Ac	Ac	H
(14)	3,5-Me_2	Ac	Ac	H
(15)		Ac	Ac	Me
(16)	3-Me	Ac	Ac	Me
(17)	3,5-Me_2	Ac	E	H
(18)		CN	E	H
(19)	3-Me	CN	E	H
(20)	3,5-Me_2	CN	E	H
(21)		CN	CN	H
(22)	3-Me	CN	CN	H
(23)	3,5-Me_2	CN	CN	H

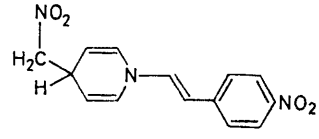
in the present case the $^-CH_2NO_2$ ion could assume that role. On the other hand, 2-methylpyridine gave a sparingly soluble orange compound (32) whose n.m.r. spectrum in deuteriochloroform showed two sets of signals which can be assigned to the two possible geometrical isomers, while in trifluoroacetic acid the appearance of a two-proton singlet, along with a down-field shift and simplification of the spectrum suggested that protonation of the exocyclic double bond had occurred to give the cation [*cf.* (2)].

The acridan (38) possessed a *cis*-acrylate group, and is apparently the kinetically preferred product since a solution slowly gave the *trans*-isomer (39). The methoxycarbonyl group of (38), in contrast to that of (39), is highly shielded by the aromatic system.

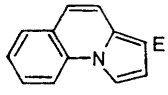
3,5-Dimethylpyridine with methyl propiolate and nitromethane also gave compound (42), the n.m.r. spectrum of which showed two AB quartets (J 13·8 and 15·6 Hz), indicating *N-trans*- and *C-trans*-acrylate



(25) R = CH_2NO_2; (26) R = OMe; (27) R = $CHAc_2$; (28) R = CHAcE; (29) R = CHCNE; (30) R = $CH(CN)_2$

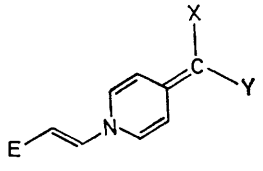


(24)

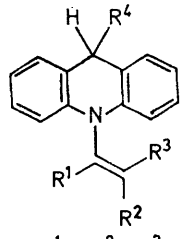


(31)

groups respectively, and a multiplet corresponding to a $CH{\cdot}CH_2$ group. The nitromethyl substituent must be



		X	Y
(32)	2-Me	H	NO_2
(33)		Me	NO_2
(34)		Ac	Ac
(35)		Ac	E
(36)	3-Me	Ac	E
(37)	3-Me	CN	E



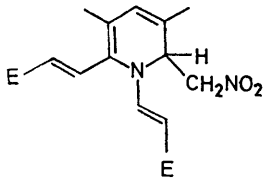
	R^1	R^2	R^3	R^4
(38)	H	H	E	CH_2NO_2
(39)	H	E	H	CH_2NO_2
(40)	E	H	E	CH_2NO_2
(41)	E	H	E	OMe

at position 2, for the methine resonance appears 1·2 p.p.m. lower than the 4-proton of the 1,4-dihydropyridine (11), but the shift of the other ring proton does not permit a distinction between structure (42) and the alternative with the acrylate side-chain at position 4. The u.v. spectrum of (42) however showed

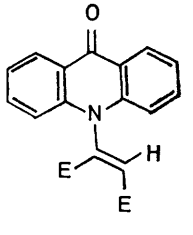
[6] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.

a bathochromic shift of 30 nm compared with that of compound (6) and is quite different from that of (11).

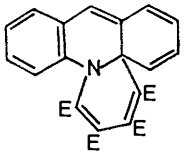
In methanol, 3,5-dimethylpyridine reacted with dimethyl acetylenedicarboxylate to give[2,7] indolizines, but on using nitromethane only 4*H*- and 9a*H*-quinolizines were isolated and these are formed in the absence of proton donors.[6] However, acridine with this diester in nitromethane gave compounds (40), (43), and (44). A trace of water, or another proton donor not necessarily nitromethane, and air could be involved in the formation of (43).[8] The vinyl proton of (40) is 0·7 p.p.m. to lower field than that of (43) so the acridan (40) has been assigned the fumarate configuration and is analogous to compound (41), the structure of which has been determined by degradation.[8] The n.m.r. spectrum of compound (44) excluded the possibility of a symmetrical structure, and showed the expected relationships to the spectrum of the corresponding tetrahydro-derivative obtained previously from 1,2,3,4-tetrahydroacridine.[9] The u.v. spectra of the compounds



(42)



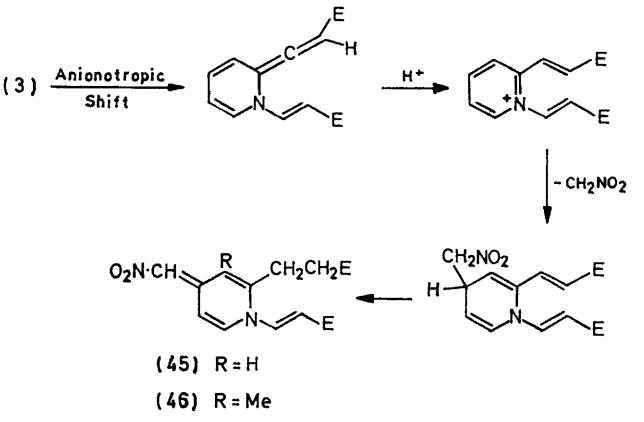
(43)



(44)

are similar although there is a bathochromic shift for the long wavelength maxima for (44). From acridine and dimethyl acetylenedicarboxylate in ether, Diels and Alder[10] isolated several compounds including a deep red substance. This was not isolated in a later investigation[8] but is probably identical with our deep red compound (44).

Cold *N*-methylmorpholine in nitromethane gave tars with the 1,2-dihydropyridines (5) and (6), but with (3) and (4), possibly by the route in Scheme 1, gave the 1,4-dihydropyridines (45) and (46). Their u.v. spectra, and n.m.r. spectra in trifluoroacetic acid, resembled those of compound (32), the expected extra methylene resonances being observed. In deuteriochloroform the n.m.r. spectrum of (46) showed the 5-proton at low field, indicating the *cis*-relationship with the nitro-group, but the spectrum of (45) showed that the absence of the 3-methyl group permitted both configurations to be adopted.



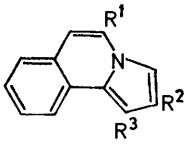
(45) R = H

(46) R = Me

SCHEME 1

Methyl propiolate and nitroethane with pyridine gave compound (12), which was oxidised by air to (33), and identified by spectral comparisons with compound (32). The corresponding reaction with isoquinoline gave the known pyrrolo[2,1-*a*]isoquinoline (47)[5] and a compound that has been assigned structure (49) provisionally (Scheme 2). Its n.m.r. spectrum could be built up from the corresponding signals expected for (25) added to those of the pyrrolo[2,1-*a*]isoquinoline nucleus [*cf.* (47) and (48)].[5] The indolizine-ester group does not deshield any proton of the indolizine system significantly, in contrast to the usual effects observed[11] which can enable its position to be located, but this must be due to the steric effect of the isoquinoline group. The u.v. spectrum of (49) can be reproduced by superimposing those of compounds (25) and (48).

Methyl propiolate with 3,5-dimethylpyridine and ethanol gave a compound analogous to (7), the n.m.r. spectrum of which showed the ethoxy-group as an ABX_3 system.[12] No adducts involving acetone, acetophenone, or diethyl malonate as proton donors could be detected



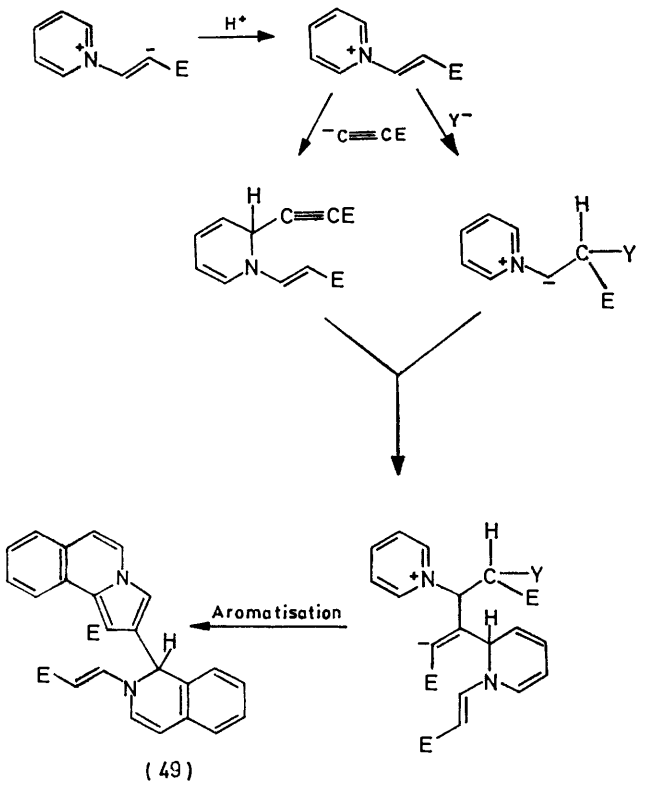
	R^1	R^2	R^3
(47)	H	E	CH_2E
(48)	Me	H	E

but this may be due to preferential attack of the sterically less demanding or more easily formed propiolate anion.

Pyridines with methyl propiolate and acetylacetone, 3-methylpentane-2,4-dione, methyl acetoacetate, methyl

[7] R. M. Acheson and G. A. Taylor, *J. Chem. Soc.*, 1960, 1691.
[8] R. M. Acheson and M. L. Burstall, *J. Chem. Soc.*, 1954, 3240.
[9] R. M. Acheson and J. K. Stubbs, *J. Chem. Soc.* (*C*), 1971, 3285.
[10] O. Diels and K. Alder, *Annalen*, 1940, **543**, 79.
[11] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1968, 1633.
[12] D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317.

cyanoacetate, or malononitrile as proton donors gave the adducts (13)—(23) and (27)—(30). Compound (14) appeared to exist as the hydrogen-bonded enol, for the Ac_2CH proton could not be detected in the n.m.r., or i.r. spectra as is reported [13,14] for strongly hydrogen bonded hydroxy-groups in quinones. Compound (29) showed two sets of signals in its n.m.r. spectrum corresponding to the two diastereoisomers. All the adducts with cyano-groups decomposed in air, sometimes within hours. Some of the adducts were interconvertible, presumably by dissociation into an anion and a pyridinium salt which could accept another anion. Heating

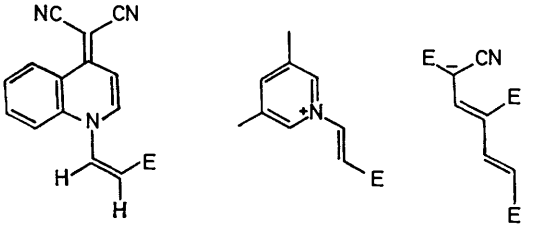


(49)

SCHEME 2

(14) or (20) in nitromethane gave (11), and (27) in methanol gave (26).

Methyl propiolate with pyridine and methyl cyanoacetate gave some of the expected dihydropyridine (18) along with compound (37), which showed that oxidation could occur *in situ*. In a number of similar reactions only the oxidised dihydropyridines (34)—(36) could be isolated. The pyridine (34) possessed an A_2B_2 system in its n.m.r. spectrum, showing that the substituents were at positions 1 and 4. The similar u.v. spectra of (34)—(36) changed to that of the pyridinium chromophore on adding a trace of acid. This change did not occur with (37), presumably because of the presence of the electron-attracting cyano-group [15,16] and a similar compound (50) from quinoline gave a quinolinium chromophore only in 72% perchloric acid. Noteworthy features of structure (50) are that the acrylate group is *cis*, the cyano-groups absorb at low frequency in the i.r., and that the 5-proton is strongly deshielded. An attempt to dehydrogenate (21) to the corresponding olefinic structure [*cf.* (32)] by 4-nitroso-*NN*-dimethylaniline gave only 4-dimethylaminophenyliminomalonodinitrile, presumably formed by dissociation of the adduct (21) to the dicyanomethanide anion which is known to give the observed product with the oxidant.



(50) (51)

On one occasion 3,5-dimethylpyridine with methyl cyanoacetate and methyl propiolate gave some dimethyl 5-cyanoisophthalate and the purple salt (51). Its n.m.r. spectrum in [$^2H_6$]dimethyl sulphoxide showed signals corresponding to the cation [*cf.* (2)], *trans*-acrylate protons, and three ester groups in a shielded environment, while the i.r. spectrum showed a long wavelength nitrile absorption. A related product has been reported [17] from dimethyl acetylenedicarboxylate, pyridine, and ethyl cyanoacetate.

EXPERIMENTAL

Instruments and procedures have been described previously.[3,18] T.l.c. was performed using precoated sheets, Polygram Sil HR/UV$_{254}$ supplied by Camlab.

All analyses for new compounds were within accepted limits for C, H, and N and are available as Supplementary Publication No. SUP 21160 (4 pp.),* which also gives details of i.r. spectra. N.m.r. and u.v. spectra are recorded in Tables 1 and 2 respectively.

General Procedure.—Unless otherwise stated, methyl propiolate (0·02 mol) was added to ether (25 ml) containing the proton donor (0·04 mol) and the pyridine (0·02 mol). After 1 week at room temperature the precipitate was collected or the solvent removed, and the residue triturated with methanol. All non-crystalline products, and filtrates from solid products were chromatographed. Variations are noted.

Nitromethane and pyridine. These afforded a small amount of yellow solid, m.p. 165—167°. Chromatography gave a

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

[13] L. J. Bellamy, 'The Infra-Red Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1964.
[14] M. St.C. Flett, *J. Chem. Soc.*, 1948, 1441.
[15] J. E. Douglas, M. W. Tabor, and J. E. Spradling, *J. Heterocyclic Chem.*, 1972, **9**, 53.
[16] Y. Kobayashi, T. Kutsuma, K. Morinaga, M. Fujita, and Y. Hanzawa, *Chem. and Pharm. Bull. (Japan)*, 1970, **18**, 2489.
[17] P. Bamfield, A. Crabtree, and A. W. Johnson, *J. Chem. Soc.*, 1965, 4355.
[18] R. M. Acheson and I. A. Selby, *J.C.S. Perkin I*, 1973, 423.

TABLE 1

N.m.r. spectra (60 MHz; τ values; J in Hz) for solutions in deuteriochloroform with Me_4Si as internal standard

Compound	Signals and assignments	CO_2Me
(3)	2-H, 4·71br; 3-H, 4·50d; 4-H, 4·00q; 5-H, 4·85m; 6-H, 3·81d; $J_{3,4}$ 6·1; $J_{4,5}$ 8; $J_{5,6}$ 8·1; H_a, 2·67d; H_b, 4·96d, J 13·8	6·31, 6·35
(4)	2-H, 5·06; 3-Me, 8·11; 4-H, 4·27d; 5-H, 4·8m; 6-H, 3·89d; $J_{4,5}$ 6; $J_{5,6}$ 8·1; H_a, 2·61d; H_b, 4·95, J 13·8	6·30, 6·34
(5)	2-, 3-, 5-H_3, 4·8—5·2m; 4-Me, 8·24; 6-H, 3·85d;[a] $J_{5,6}$ 7·8; H_a, 2·67d; H_b, 5·01d, J 13·8	6·32, 6·37
(6) [3,b]	2-H, 5·06; 3-Me, 8·25; 4-H, 4·29; 5-Me, 8·09; 6-H, 4·03; H_a, 2·57d; H_b, 4·97d, J 13·4	6·24, 6·28
(8)	2-H, 5·2br; 3-Me, 8·25;[c] 4-H, 4·34; 5-Me, 8·35;[c] 6-H, 4·10; 2-CH, 6·45m; H_a, 2·83d; H_b, 5·11d, J 13·5	6·4
(9)	2,6-H_2, 3·60d; 3,5-H_2, 5·11q; 4-H, 6·2m; 4-CH_2, 5·65d; $J_{2,3}$ 8; $J_{3,4}$ 4·0; $J_{4,4'}$ 7·2; H_a, 2·76d; H_b, 4·84d, J 13·8	6·13
(10)	2-H, 3·79; 3-Me, 8·26; 4-H, 6·35m; 5-H, 5·13q; 6-H, 3·67d; 4-CH_2, 5·63d; $J_{4,5}$ 4·2; $J_{5,6}$ 8·5; $J_{4,4'}$ 5·7; H_a, 2·81d; H_b, 4·92d, J 13·6	6·36
(11)	2,6-H_2, 3·81; 3,5-Me_2, 8·22; 4-H 6·54t; 4-CH_2, 5·55d; J 4·5; H_a, 2·84d; H_b, 4·95d, J 14·1	6·37
(12)	2,6-H_2, 3·56d; 3,5-H_2, 5·15q; 4-H 6·25m; 4-C*H*, 5·55m, ΣJ 24; 4-CMe, 8·49d, J 7; $J_{2,3}$ 8; $J_{3,4}$ 4; H_a, 2·75d; H_b, 4·83d, J 13·7	6·28
(13)	2-H, 3·87d; 3-Me, 8·42; 4-H, 5·80br; 5-H, 5·25q; 6-H, 3·76q; 4-C*H*, 6·30; 4-CAc_2, 7·84; $J_{3,6}$ 1·8; $J_{4,5}$ 3·6; $J_{5,6}$ 7·9; H_a 2·77d; H_b, 4·95d, J 13·8	6·35
(14)	2,6-H_2, 3·87; 3,5-Me_2, 8·41; 4-H 5·95; 4-CAc_2, 7·79, 7·95; H_a, 2·79d; H_b, 4·97d, J 13·5	6·35
(15)	2,6-H_2, 3·72d; 3,5-H_2, 5·39q; 4-H, 5·82t; 4-CMe, 8·67; 4-CAc_2 7·93, 7·93; $J_{2,3}$ 8·1; $J_{3,4}$ 3·9; H_a, 2·84d; H_b, 4·95, J 13·5	6·35
(16)	2-H, 3·81d; 3-Me, 8·50; 4-H, 5·53d; 4-CMe, 8·70; 4-CAc_2, 7·87, 7·93; 5-H, 5·35q; 6-H, 3·67q; $J_{3,6}$ 1·5; $J_{4,5}$ 4·6; $J_{5,6}$ 8·0; H_a, 2·82d; H_b, 4·95d, J 13·7	6·36
(17)	2,6-H_2, 3·89br; 3,5-Me_2, 8·30, 8·35; 4-H, 4-CH, 6·4m; Ac, 7·80; H_a, 2·73d; H_b, 5·01, J 13·5	6·40, 6·40
(18)	2,6-H_2, 3·55d; 3,5-H_2, 5·09q; 4-H, 6·2m; 4-CH, 6·51d, J 5·1; $J_{2,3}$ 7·8; $J_{3,4}$ 3·4; H_a, 2·77d; H_b, 4·83d, J 13·7	6·20, 6·33
(19)	2-H, 3·70; 3-Me, 8·25;4-H, 6·4m; 4-CH, 6·4; 5-H, 5·2m; 6-H, 3·57q; $J_{2,6}$ 1·2; $J_{5,6}$ 9·0; H_a, 2·81d; H_b, 4·88d, J 13·8	6·21, 6·29
(20)	2,6-H_2, 3·72; 3,5-Me_2, 8·18, 8·32; 4-H, 4-CH, 6·3m; H_a, 2·80d; H_b, 4·89d, J 13·7	6·26, 6·38
(21) [d]	2,6-H_2, 3·03d; 3,5-H_2, 5·06q; 4-H, 6·1; 4-C*H*, 6·42; $J_{2,3}$ 7·2; $J_{3,4}$ 4·2; H_a, 2·55d; H_b, 4·56d, J 13·8	6·42
(25)	Ar-H_4, 2·75—3·05m; 1-H 4·45;[e] 3-H, 3·64d;[a] 4-H, 4·00d; 1-CH_2, 5·42q, 5·68q, J 11·4; $J_{1,1'}$ 6·9; $J_{1,3}$ 1·2; $J_{3,4}$ 7·6; H_a, 2·60d; H_a, 4·74d, J 13·8	6·35
(26) [5,b]	Ar-H_4, 2·06—2·95m; 1-H, 3·93; 3-H, 3·40d; 4-H, 4·08d; $J_{3,4}$ 7·5; H_a, 2·40d; H_b, 4·53d, J 14·5; 1-OMe, 6·99	6·27

TABLE 1 (*Continued*)

Compound	Signals and assignments	CO_2Me
(27)	Ar-H_3, 2·75—3·10m; 1-H, 4·46q; 1-CH, 5·60d, J 8·8; 3-H, 3·62q; 4-H, 3·95d; 1-CAc_2, 7·83, 8·22; $J_{1,3}$ 1·2; $J_{3,4}$ 9·5; H_a, 2·60d; H_b, 4·94d, J 13·7	6·36
(28)	Ar-H_4, 2·7—2·9m; 1-H, 4·48q; 1-CH, 5·80d, J 9·4; 3-H, 3·56q; 4-H, 3·89d; $J_{1,3}$ 1·3; $J_{3,4}$ 7·6; H_a, 2·51d; H_b, 4·87d, J 13·5; 1-CAc, 8·16	6·29, 6·31
(29)	Ar-H_4, 2·70—2·95m; 1-H, 4·56d; 1-CH, 6·11d, J 6·3; 4-H, 4·06d; $J_{3,4}$ 7·4 set (a): 3-H, 3·56d; H_a, 2·55d; H_b, 4·80d, J 13·8 set (b): 3-H, 3·64d; H_a, 2·61d, H_b, 4·86d, J 13·8	6·23, 6·35
(30)	Ar-H_4, 2·70m, 1-H, 4·59d; 1-CH, 5·90d, J 6·6; 3-H, 3·55d; 4-H, 3·97d; $J_{3,4}$ 7·5; H_a, 2·53d; H_b, 4·74d, J 13·9	6·32
(33) [f]	2,6-H_2, 0·76d; 3,5-H_2, 1·60d; 4-CH, 3·85q; 4-CMe, 7·87d, J 7; $J_{2,3}$ 6·6; H_a, 1·42d; H_b, 2·89d, J 14·1	5·92
(34)	2,6-H_2, 2·81d;[a] 3,5-H_2, 2·63d;[a] $J_{2,3}$ 8; H_a, 2·48d; H_b, 4·13d, J 13·8; 4-CAc_2, 7·68, 7·68	6·19
(35)	Ar-H_4, 2·4—2·7m; H_a, 2·48d; H_b, 4·14d, J 14·0; 4-CAc, 7·72	6·20, 6·20
(36)	2-H, 2·85; 3-Me, 8·07; 5-H, 1·89d; 6-H, 2·8d; $J_{5,6}$ 8·2; H_a, 2·47d; H_b, 4·10d, J 14·0; 4-CAc, 7·71	6·20, 6·20
(37) [f]	2,6-H_2, 0·90br; 3-Me, 7·22; 4-CH, 4·25; 5-H, 1·55d; $J_{5,6}$ 6; H_a, 1·48d; H_b, 2·89d, J 14·5	5·93, 5·98
(38)	Ar-H_8, H_a, 2·65—3·05m; 9-H, 5·25m; 9-CH_2, 5·45m; H_b, 4·52d, $J_{a,b}$ 9	6·71
(39)	Ar-H_8, 2·3—2·9m; 9-H, 5·31q; ΣJ 15; 9-CH_2, 5·66m; H_a, 1·85d; H_b, 4·22d; J 13·9	6·30
(40)	Ar-H_6, 2·70—3·25m; 4,5-H_2, 3·43q; 9-H, 5·55q; ΣJ 15; 9-CH_2, 5·52m; vinyl-H, 2·56; $J_{3,4}$ 7·8; $J_{2,4}$ 2·2	6·29, 6·42
(42)	3-Me, 7·98; 4-H, 4·09; 5-Me, 8·06; 6-H, 5·32q; ΣJ 13·5; 6-CH_2, 5·82m; H_a, 2·77d; H_b, 5·03d; J 13·8; H_c, 2·46d; H_d, 4·80d, J 15·6	6·30, 6·40
(43)	Ar-H_2, 2·35m; Ar-H_4, 2·6—2·85m; 1,8-H_2, 1·52d;[a] vinyl-H, 3·26, $J_{1,2}$ 8	6·08, 6·36
(44)	Ar-H_2, 2·9m; vinyl-H_2, 3·81m; vinyl-H_2, 4·05m; 5-H, 3·42d; 7-H, 3·10m, ΣJ 14·4; 9-H, 3·28; $J_{5,6}$ 8·4	6·12, 6·20 6·33, 6·37
(45) [f]	2-CH_2, 6·35t; 2-CH_2CH_2, 6·83t, J 7·5; 3-H, 1·67; 4-CH_2, 4·05; 5-H, 1·78d; 6-H, 1·04d; $J_{5,6}$ 6·5; H_a, 1·37d; H_b, 3·03d, J 14·2	5·91, 6·12
(46)	2-CH_2, 6·87m; 2-CH_2CH_2, 7·42m; 3-Me, 7·99; 5-H, 1·62d; 6-H, 2·59d; $J_{5,6}$ 8·1; vinyl-H, 3·14; H_a, 2·01d; H_b, 3·97d, J J 13·6	6·22, 6·32
(46) [f]	2-CH_2, 6·30t; 2-CH_2CH_2, 7·05t, J 7; 3-Me, 7·32; 4-CH_2, 4·07; 5-H, 1·92d; 6-H, 1·24d; $J_{5,6}$ 6·1; H_a, 1·38d; H_b, 3·13d, J 13·5	5·97, 6·16
(47) [5,b]	Ar-H_3, 2·35—2·80m; 1-CH_2, 5·49; 3-H, 2·30; 5-H, 2·49d; 6-H, 3·33d; 10-H, 1·99q; $J_{5,6}$ 9·5; $J_{9,10}$ 8·2; $J_{8,10}$ 1·1	6·18, 6·31
(48) [5,b]	Ar-H_4, 2·30—2·90m; 2-H 2·83d; 3-H, 2·71d; 5-Me, 7·49; 6-H, 3·24; 10-H, 0·18d;[a] $J_{2,3}$ 3·1	6·07
(49)	Ar-H_3, 2·5m; Ar-H_5, 2·7—2·9m; 3-H, 2·6; 5-H, 3·18d; 10-H, 0·98d; 1′-H, 3·19; 3′-H, 3·46d; 4′-H, 4·13d; $J_{5,6}$ 7·5; $J_{9,10}$ 8·5; $J_{3',4'}$ 7·7; H_a, 2·37d; H_b, 4·75d, J 14·0	5·82, 6·36

TABLE 1 (*Continued*)

Compound	Signals and assignments	CO_2Me
(50) [b,d]	Ar-H_2, 2·36m; 2-H, 3·18d; 3-H, 1·97d; 5-H, 2·13d,[a] 8-H, 1·06d;[a] $J_{2,3}$ 7·6; $J_{5,6}$ 7·2; $J_{7,8}$ 8; H_a, 2·33d; H_b, 3·61d, J 8·8	6·38
(51)	2,6-H_2, 0·87; 3,5-Me_2, 7·52: 4-H, 1·58br; 1′-H, 1·70d; 2′-H, 2·86; $J_{1',2'}$ 14; anion: H(1), 2·00; H(1), 1·72d; H(1), 3·82d, J 15	6·22, 6·48 6·48, 6·48
(A) [g]	2-H, 4·61; 3-Me, 8·25; 4-H, 4·13; 5-Me, 8·12; 6-H, 3·83; H_a, 2·65d; H_b, 4·77d, J 13·8; O·CH_2, 6·83q, 6·90q; O·$CH_2C\underline{H}_3$, 8·93, J 6·9	6·41
(B) [b,g]	2-H, 1·13; 6-H, 0·69br; 7-Me, 7·48; 8-H, 2·32br; 9-Me, 7·48; vinyl-H, 0·85	6·01, 6·06
(C) [g]	3-H, 1·17; 4,6-H_2, 1·56, J 1·5	60·5, 6·05
(D) [g]	2,4-H_2, 2·32d; 3,5-H_2, 3·42d; J 9; NMe_2, 6·89, 6·89	

[a] With further splitting. [b] At 100 MHz. [c] Assignments could be reversed. [d] In $(CD_3)_2SO$. [e] Six lines. [f] In CF_3COOH. [g] (A) 2-ethoxy-1,2-dihydro-1-(trans-2-methoxycarbonylvinyl)-3,5-dimethylpyridine; (B) 3-[(E)-2-cyano-2-methoxycarbonylvinyl]-1-methoxycarbonyl-7,9-dimethylquinolizin-4-one; (C) dimethyl 5-cyanoisophthalate; (D) 4-dimethylaminophenyliminomalononitrile.

TABLE 2

U.v. spectra

Compound	Solvent [a]	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$)
(3)[2]	E	239 (0·79), 297 (0·89), 342 (1·20)
(5)	M,A	223 (2·36), 248 (1·56), 254 (1·25), 260 (1·04), 227infl (0·68)
(6)	M	212 (1·71), 225infl (1·53), 261 (0·36), 267 (0·37), 274 (0·28)
	A	220 (1·57), 268 (0·59)
(10)	M,A	223 (2·36), 248 (1·56), 254 (1·25), 260 (1·04), 277infl (0·68)
(11)	M	212 (1·71), 225infl (1·53), 261 (0·36), 267 (0·37), 274 (0·28)
	A	220 (1·57), 268 (0·59)
(14)	M	238 (1·52), 269 (1·06), 275 (1·07), 283infl (0·82)
	A	238 (1·52), 268 (1·30)
(15)	M	208 (0·83), 232 (1·10), 256 (0·61), 263 (0·55), 312 (0·66)
	A	208 (0·86), 233(0·52), 256 (1·00), 262 (0·93), 270infl (0·77)
(16)	M	212 (1·03), 229 (1·33), 255infl (0·60), 263 (0·59), 270 (0·55), 291 (0·46)
	A	228 (1·28), 263 (0·81), 270infl (0·73), 287 (0·47)
(17) [b]	M	229 (1·42), 260 (0·45), 267 (0·44), 275 (0·33)
	A	229 (1·42), 267 (0·66), 275infl (0·51)
(18)	M	209 (0·74), 232 (1·35), 250infl (0·75), 256infl (0·57), 262infl (0·42), 330 (0·31)
	A	211 (0·85), 232 (1·30), 250infl (0·99), 256infl (0·95), 261infl (0·82), 273infl (0·38)
(21)	M	231 (1·27), 250infl (0·67), 256 (0·51), 262 (0·34), 338 (0·15)
	A	232 (1·21), 250infl (0·85), 255 (0·77), 261 (0·55)
(25)	M,A,	242 (1·40), 335 (2·62)
(26) [5]	M	209 (2·07), 240 (1·41), 302infl (1·46), 334 (3·19)
(27)	M	240 (1·53), 296 (2·45), 332 (3·26)
	A	251 (4·54), 290infl (1·44), 355 (0·51)
(28)	M	243 (1·36), 255 (1·55), 265 (2·03), 272infl (1·44), 331 (2·29), 341infl (2·00)
	A	217infl (1·78), 255 (3·50), 304 (1·03), 354 (0·38)
(29)	M	240 (1·20), 303infl (1·31), 332 (2·82)
	A	249 (3·45), 303 (1·25), 355 (0·45)
(30)	M	213 (1·42), 241 (1·29), 331 (2·75), 340infl (2·42)
	A	216 (1·33), 250 (3·44), 304 (1·21), 354 (0·45)
(32)	M	266 (0·98), 456 (6·35)
	A	245 (0·93), 270infl (0·81), 364 (0·25)
(33)	M	250 (1·11), 265 (1·05), 463 (3·44)
(34)	M	230 (0·83), 296 (0·53), 426infl (2·69), 438 (2·86)
	A	235 (1·02), 277 (1·23), 359 (0·60)
(35)	M	250 (1·02), 418infl (1·10), 429 (1·12)
	A	259 (1·40), 259 (1·40), 352 (0·50)
(36)	M	265 (1·45), 390infl (0·91), 415 (1·38), 443 (1·64)
	A	256 (1·66), 335 (0·31)
(37)	M	240 (0·58), 275 (0·37), 413 (2·06)
(38)	M	213 (2·36), 265 (1·11), 291infl (0·65), 333 (0·71)
	A	213 (2·34), 235infl (0·58), 279 (1·36), 303infl (0·77)
(40)	M,A,	213 (1·69), 239infl (0·82), 272 (1·56)
(42)	M,A,	225 (1·31), 280 (1·54), 310 (1·71), 369infl (0·81)
(44)	M,A,	209 (2·55), 230 (2·61), 272 (1·40), 300infl (1·15), 357 (1·08), 470 (0·08)
(45)	M	267 (0·97), 454 (6·10)
	A	244 (0·87), 270infl (0·76)
(46)	M	212·5 (1·49), 268 (1·04), 450 (5·35)
	A	215 (1·57), 245 (0·82), 285 (0·72)
(47) [5]	M	216 (2·48), 257infl (4·78), 264 (6·73), 298 (0·47), 311 (0·50), 324 (0·50), 340infl (0·27)
(48) [5]	M	218 (3·06), 243 (1·36), 266 (3·01), 275 (4·92), 313infl (0·82), 323 (1·02), 337 (0·99), 353 (0·85)
(49)	M,A,	209 (4·64), 245infl (2·54), 248 (2·66), 253infl (2·51), 270infl (3·3), 278 (3·88) 341 (3·22)
(50)	M,A,	211 (2·46), 228 (2·12), 258 (0·57), 273infl (0·72), 282 (0·87), 295infl (0·68), 415 (3·59), 433 (4·39)
	Q	246 (1·5),[c] 331 (0·4) [c]
(51)	M	236 (2·58), 275 (0·69), 307 (1·35), 409 (3·49)
	A	221 (1·88), 270 (1·75), 355 (0·27)
(A) [d]	M	220 (1·12), 230 (1·39)
	A	226 (1·39)
(B) [d]	M,A,	232 (1·54), 253infl (0·90), 268 (0·90), 304 (1·26), 313infl (1·16), 334 (0·51), 483 (3·47)
(D) [d]	M	251 (0·75), 289 (0·49), 320infl (0·33), 489 (2·29)
	A	220 (0·72), 245 (0·36), 287 (0·45), 491 (1·94)

[a] M, MeOH; A, MeOH + 1 drop of $HClO_4$; E, EtOH; Q, MeOH–72% $HClO_4$ (1 : 3 v/v). [b] For a mixture of 64% (17) and 36% (8). [c] Optical densities recorded. [d] See footnote *g*, Table 1.

yellow gum identified as 1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-4-nitromethylpyridine (9) by n.m.r.

With 0·02 mol of nitromethane, only methyl [1,2-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-2-pyridyl]propiolate (3) (20%) was obtained.

Nitromethane and 3-*methylpyridine.* 1,4-*Dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3-*methyl*-4-*nitromethylpyridine* (10) (8·8%) was obtained as yellow needles (from ether–chloroform), m.p. 102—105°.

With 0·02 mol of nitromethane, methyl [1,2-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-3-methyl-2-pyridyl]propiolate (4) (5·8%) was formed.

Nitromethane and 3,5-*dimethylpyridine.* 1,4-*Dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3,5-*dimethyl*-4-*nitromethylpyridine* (11) (6·5%) was obtained as yellow rods (from methanol), m.p. 140—142·5°.

With 0·1 mol of each reagent in ether (50 ml), only methyl [1,2-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-3,5-dimethyl-2-pyridyl]propiolate (6) was formed, identical (i.r. and n.m.r.) with an authentic sample.

The acetylene and the pyridine (0·05 mol each), and nitromethane (0·2 mol) in ether (25 ml) gave a mixture of (11) and (6). The filtrate was discarded, and the mixture recrystallised from methanol to give a pure sample of (11). The mother liquors from the recrystallisation gave 1,2-*dihydro*-1,6-*bis*-(trans-2-*methoxycarbonylvinyl*)-3,5-*dimethyl*-2-*nitromethylpyridine* (42) (0·65%) as yellow prisms (from methanol), m.p. 124—126·5°, *m/e* 336 (M^+, 4%), 305 (3, $M - 31$), 277 (17, $M - CO_2Me$), 276 (100, $M - CH_2NO_2$), 230 (11), 216 (40), 160 (20), 159 (11), 158 (50), 157 (16), 156 (14), 146 (32), 144 (11), 131 (23), 130 (17), and 117 (12), *m** 276 (336 → 305), 227 (336 → 276), 169 (276 → 216), and 131 (191 → 160).

Nitromethane and 4-methylpyridine. The only compound isolated in each of three experiments was methyl [1,2-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-4-methyl-2-pyridyl]propiolate (5) (*ca.* 74%).

Nitromethane and 2-methylpyridine. 1,4-*Dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-2-*methyl*-4-*nitromethylene-pyridine* (32) was isolated as red rods (from methanol–chloroform), m.p. 187—190°, *m/e* 237 (13%), 236 (M^+, 80), 220 (12), 206 (100), 205 (12), 177 (81), 161 (7), 146 (29), 131 (24), 130 (46), 118 (24), 117 (25), 104 (10), and 91 (31), *m** 180 (236 → 206), 146 (177 → 161), and 95 (177 → 130).

Nitromethane and quinoline. Chromatography gave methyl pyrrolo[1,2-*a*]quinoline-3-carboxylate (31) (2·6%) with spectra identical with those reported.[5]

Nitromethane and isoquinoline. 1,2-*Dihydro*-2-(trans-2-*methoxycarbonylvinyl*)-1-*nitromethyl-isoquinoline* (25) (21%) was obtained as yellow needles (from methanol), m.p. 130—132°.

Nitromethane and acridine. Acridine (1·79 g, 0·01 mol) and methyl propiolate (1·68 g, 0·02 mol) in nitromethane (25 ml) were refluxed for 4 h, cooled, evaporated, and the residue chromatographed. The first pale yellow band on rechromatography and recrystallisation gave acridine, 10-(cis-2-*methoxycarbonylvinyl*)-9-*nitromethylacridan* (38), as yellow crystals (from acetonitrile–ether), m.p. 182—185°, and 9-nitromethylacridan, as yellow prisms (from methanol), m.p. 149—151° (lit.,[19] 148—149°), $\nu_{max.}$ 3380, 1618, 1607, 1589, 1538, 1482, 1458, and 1428 cm^{-1}.

The second, yellow, band from the first column gave more (38) (total yield, 8%).

A solution of (38) in $CDCl_3$ after 1 week showed only signals attributable to 10-(*trans*-2-methoxycarbonylvinyl)-9-nitromethylacridan (39), a brown oil, $\nu_{max.}$ 1705br, 1630, 1607, 1595, 1582, 1555, 1499, 1481, 1460, and 1439 cm^{-1}; attempted purification failed.

Dimethyl Acetylenedicarboxylate with Nitromethane and 3,5-Dimethylpyridine.—This reaction gave tetramethyl 7,9-dimethyl-9a*H*-quinolizine-1,2,3,4-tetracarboxylate. T.l.c. of the filtrate alongside authentic specimens showed only this compound and the 4*H*-isomer.

Dimethyl Acetylenedicarboxylate with Nitromethane and Acridine.—The acetylene (2·84 g, 0·02 mol) was added to acridine (1·79 g, 0·01 mol) and nitromethane (5 ml) in ether (15 ml). After 4 days evaporation and trituration of the residue with toluene gave dimethyl 9-oxoacridan-10-ylmaleate (43) (40 mg, 1·2%) as pale green crystals (from methanol), m.p. 217—220° (lit.,[8] 222—223°), *m/e* 338 (28%), 337 (M^+, 100), 278 (37), 277 (17), 246 (29), 234 (40), 221 (12), 219 (45), 191 (15), 190 (16), and 91 (28), *m** 229·5 (337 → 278), 218 (278 → 246), 205 (234 → 219), 197 (278 → 234), 166·5 (219 → 191), and 163·5 (221 → 190).

Chromatography of the filtrate gave an orange band yielding acridine and an oil which solidified with methanol to give *dimethyl 9-nitromethylacridan-10-ylfumarate* (40) (330 mg, 8·8%) as orange prisms (from ether–acetonitrile), m.p. 131—134°.

The second band (red) gave the *tetramethyl pyrido*-[2,1-e]*acridine*-1,2,3,4-*tetracarboxylate* (44) (260 mg, 6·3%), as maroon crystals (from methanol–chloroform), m.p. 153—156°, *m/e* 464 (19%), 463 (M^+, 44), 405 (30), 404 (100), 373 (14), 372 (8), 348 (11), 344 (23), 341 (8), 313 (10), 286 (15), 228 (15), 227 (18), and 179 (12), *m** 352·5 (463 → 404), 343 (404 → 373), and 312 (372 → 341).

Nitromethane with Compound (3).—Compound (3) (1·44 g) was left at room temperature with *N*-methylmorpholine (0·2 ml) in nitromethane (50 ml) for 3 weeks. Evaporation and trituration with methanol gave *methyl* 3-[1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-4-*nitromethylene*-2-*pyridyl*]*propionate* (45) (400 mg, 22%), as orange rods (from methanol–chloroform), m.p. 155—158°.

Nitromethane with Compound (4).—Compound (4) (300 mg) with *N*-methylmorpholine (0·3 ml) in nitromethane (25 ml) as above gave *methyl* 3-[1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3-*methyl*-4-*nitromethylene*-2-*pyridyl*]*propionate* (46) (92 mg, 25%) as orange platelets (from methanol), m.p. 157—160°.

Similar reactions with compounds (5) and (6) gave tars.

Nitroethane and Pyridine.—Chromatography gave a gum which deposited yellow crystals of crude 1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-4-(1-nitroethyl)pyridine (12), m.p. 68—72°.

In methanol exposed to the air, compound (12) gave a precipitate of 1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-4-(1-*nitroethylidene*)*pyridine* (33), as red-brown microcrystals, m.p. 218—220°, *m/e* 236 (M^+, 46%), 206 (42), 190 (21), 189 (100), 188 (25), 163 (17), and 106 (17), *m** 151·5 (236 → 189).

Nitroethane and Isoquinoline.—Methyl 1-methoxycarbonylmethylpyrrolo[2,1-a]isoquinoline-2-carboxylate (47) crystallised and was identical (u.v., i.r., and n.m.r.) with an authentic sample. Chromatography gave a product tentatively assigned as methyl 2-[1,2-dihydro-2-(*trans*-2-methoxycarbonylvinyl)isoquinolin-1-yl]pyrrolo[2,1-*a*]-isoquinoline-1-carboxylate (49) (5·5%), as white platelets (from methanol–chloroform), m.p. 220·5—222·5°, *m/e* 438 (M^+, 55%), 424 (23), 423 (78), 391 (14), 370 (100), 347 (35), 321 (40), 320 (30), 310 (100), and 267 (26), *m** 376·5 (438 → 406), 361·5 (423 → 391), 328 (438 → 379), and 318 (379 → 347).

Diethyl Malonate, Acetone, and Acetophenone with Pyridines.—In no case was any new compound obtained in reaction between a variety of pyridines and these proton-donors on using the general procedure. Isoquinoline gave the pyrrolo[2,1-*a*]isoquinoline (47) and 3,5-dimethylpyridine gave the ethynyl adduct (6) (using diethyl malonate), and dimethyl 5,7-dimethylpyrrolo[2,1,5-*cd*]indolizine-2,4-dicarboxylate (using acetone).

Ethanol and 3,5-Dimethylpyridine.—2-*Ethoxy*-1,2-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3,5-*dimethylpyridine* (41%)

[19] F. Kröhnke and H. L. Honig, *Annalen*, 1959, **624**, 97.

was obtained as pale yellow crystals, m.p. 60—64°, which decomposed on attempted recrystallisation.

Acetylacetone and Pyridine.—4-*Diacetylmethylene*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)*pyridine* (34) was precipitated as yellow micro-rods (from methanol), m.p. 178—181°. The filtrate gave first tris(acetylacetonato)-aluminium (0·5 g), as large white crystals (from methanol), m.p. 192—193° (lit.,[20] 192—194°) and more (34) (total 5%).

Acetylacetone and 3-*Methylpyridine.*—4-Diacetylmethyl-1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-3-methylpyridine (13) (48%) was isolated as purple crystals, m.p. 95—99°, decomposing on attempted recrystallisation.

Acetylacetone with 3,5-*Dimethylpyridine.*—Reaction gave 4-*Diacetylmethyl*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3,5-*dimethylpyridine* (14) (59%), as pale yellow crystals (from nitromethane), m.p. 119—122°, *m/e* 291 (M^+, 13%), 276, (15), 193 (23), 192 (100), 178 (23), 108 (18), 107 (87), 106 (62), 100 (62), and 92 (23). Heating (14) in nitromethane caused partial conversion into (11).

Acetylacetone and Isoquinoline.—1-*Diacetylmethyl*-1,2-*dihydro*-2-(trans-2-*methoxycarbonylvinyl*)*isoquinoline*(27)(51%), was isolated as white needles (from toluene–chloroform), m.p. 127—130°. Refluxing (27) in methanol for 15 min gave (26) with the reported spectra.

3-*Methylpentan*-2,4-*dione with Pyridine.*—Reaction gave 4-(1,1-*diacetylethyl*)-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)*pyridine* (15) (48%), as white crystals (from toluene–petroleum), m.p. 72·5—75·5°.

3-*Methylpentan*-2,4-*dione with* 3-*Methylpyridine.*—Reaction gave 4-(1,1-*diacetylethyl*)-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3-*methylpyridine* (16) (42%), as pale yellow crystals (from petroleum–toluene), m.p. 96—99°.

Methyl Acetoacetate and Pyridine.—4-*Acetyl*(*methoxycarbonyl*)*methylene*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)*pyridine* (35) was obtained as yellow platelets (from methanol–chloroform), m.p. 204·5—205·5°, *m/e* 277 (M^+, 35%), 263 (15), 262 (100), 246 (17), 232 (10), 218 (4), 204 (43), 203 (11), 163 (19), 120 (9), 104 (12), and 90 (9), *m** 248 (277 ⟶ 262), 205·5 (262 ⟶ 232), 204·5 (232 ⟶ 218), 179·5 (232 ⟶ 204), and 169 (246 ⟶ 204). Further (36) (total yield 1·9%) was obtained by chromatography.

Methyl Acetoacetate and 3-*Methylpyridine.*—4-*Acetyl*(*methoxycarbonyl*)*methylene*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3-*methylpyridine* (36) (1·2%) was isolated as yellow lenticular plates (from methanol), m.p. 189—191°.

Methyl Acetoacetate and 3,5-*Dimethylpyridine.*—4-Acetyl(methoxycarbonyl)methyl-1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-3,5-dimethylpyridine (17), and its 2-acetyl(methoxycarbonyl)methyl-1,2-dihydro-isomer (8) were filtered off as a 2 : 1 mixture (33%), as a pale cream powder, m.p. 106—110°. Attempted separation induced decomposition.

Methyl Acetoacetate and Isoquinoline.—1-*Acetyl*(*methoxycarbonyl*)*methyl*-1,2-*dihydro*-2-(trans-2-*methoxycarbonylvinyl*)*isoquinoline* (28) (29%) was isolated as white needles (from toluene–petroleum), m.p. 95—97°.

Methyl Cyanoacetate and Pyridine.—4-Cyano(methoxycarbonyl)methyl-1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)pyridine (18) (25%) was obtained as a white solid, m.p. 69—73°. Attempted recrystallisation or keeping *in vacuo* caused decomposition.

[20] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1921, 1058.

Methyl Cyanoacetate and 3-*Methylpyridine.*—Reaction gave 4-cyano(methoxycarbonyl)methyl-1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-3-methylpyridine (19) (47%) as unstable [*cf.* (18)] purple crystals, m.p. 95—99°. The filtrate deposited 4-*cyano*(*methoxycarbonyl*)*methylene*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3-*methylpyridine* (37) (0·2%) as yellow platelets (from methanol–chloroform), m.p. 239—242°, *m/e* 275 (18%), 274 (M^+, 94), 244 (23), 243 (100), 242 (18), 218 (12), 217 (12), 216 (63), 215 (23), 191 (18), 131 (12), 130 (12), and 129 (12), *m** 215 (274 ⟶ 243).

Methyl Cyanoacetate and 3,5-*Dimethylpyridine.*—(i) The precipitate consisted of a cream powder, m.p. 96—99° and a smaller amount of hard, pale yellow crystals, m.p. 87—90° (crude). The two crystal types were separated by hand, and shown to have the same n.m.r. spectra, assigned to 4-cyano(methoxycarbonyl)methyl-1,4-dihydro-1-(*trans*-2-methoxycarbonylvinyl)-3,5-dimethylpyridine (20) (total yield 56%). Heating (20) for 10 min in nitromethane gave, on cooling, a precipitate of compound (11), and in methanol the salt (51).

(ii) Repeating the experiment gave in 2 days a purple precipitate which afforded orange plates (51) (from methanol), m.p. 129·5—131°.

Chromatography gave first a red band, probably 3-[(E)-2-*cyano*-2-*methoxycarbonylvinyl*]-1-*methoxycarbonyl*-7,9-*dimethylquinolizin*-4-*one* (0·16%), as cerise rods (from methanol–chloroform), m.p. 239—242°, *m/e* 341 (24%), 340 (M^+, 100), 312 (15), 309 (31), 282 (15), 281 (76), 277 (16), 253 (11), 249 (19), 222 (11), 221 (13), 194 (11), 193 (23), and 179 (10), *m** 281 (340 ⟶ 309), 249 (309 ⟶ 277), 253 (312 ⟶ 281), 232 (340 ⟶ 281), 221 (281 ⟶ 249), and 193 (253 ⟶ 221).

The next (pale red) band gave dimethyl 5-cyanoisophthalate (1·0%) as colourless rods (from toluene–petroleum), m.p. 173—175·5° (lit.,[21] 174·5—175°), $\nu_{max.}$ 2238, 1740infl, 1729, 1445, 1440infl, and 1431 cm^{-1}, *m/e* 219 (M^+, 25%), 218 (4), 189 (12), 188 (100), 160 (19), 145 (10), and 101 (15), *m** 217 (219 ⟶ 218), 161·5 (219 ⟶ 188), and 136·5 (188 ⟶ 160).

Methyl Cyanoacetate and Isoquinoline.—Reaction gave 1-*cyano*(*methoxycarbonyl*)*methyl*-1,2-*dihydro*-2-(trans-2-*methoxycarbonylvinyl*)*isoquinoline* (29) (80%) as white needles, m.p. 110—116°. Recrystallisation (from methanol) gave white needles, m.p. 110—112·5° with the same n.m.r. but different i.r. spectrum.

Malononitrile and Pyridine.—4-*Dicyanomethyl*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)*pyridine* (21) (41%), was isolated as a pale grey powder, m.p. 100—104°. The compound decomposed on attempted recrystallisation or warming. Compound (21) (334 mg) was boiled with 4-nitroso-*NN*-dimethylaniline (300 mg) in methanol (35 ml) for 10 min. The solvent was removed and the chloroform-soluble fraction of the residue was chromatographed to give 4-dimethylaminophenyliminomalononitrile (30 mg) as scarlet needles (from toluene–petrol), m.p. 159—166° (lit.,[22] 167°), $\nu_{max.}$ 2210, 2190, 1615, 1548, 1452, and 1440 cm^{-1}, *m/e* 198 (M^+, 74%), and 197 (100), *m** 196 (198 ⟶ 197).

Malononitrile and 3-*Methylpyridine.*—4-*Dicyanomethyl*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3-*methylpyridine* (22) (7·5%) was isolated as brownish crystals, m.p. 82—84°,

[21] E. W. Crandall and L. Hains, *Org. Preparations and Procedures*, 1969, **1**, 147.

[22] D. M. W. Anderson and F. Bell, *J. Chem. Soc.*, 1959, 3708.

which decomposed on attempted recrystallisation or on storing *in vacuo*.

Malononitrile and 3,5-*Dimethylpyridine.*—4-*Dicyanomethyl*-1,4-*dihydro*-1-(trans-2-*methoxycarbonylvinyl*)-3,5-*dimethylpyridine* (23) (27%) was obtained as a khaki powder, m.p. 78—80°. The compound decomposed rapidly even *in vacuo*.

Malononitrile and Isoquinoline.—1-*Dicyanomethyl*-1,2-*dihydro*-2-(trans-2-*methoxycarbonylvinyl*)*isoquinoline* (30) (80%) was isolated as cream crystals (from methanol), m.p. 132·5—137·5°.

Malononitrile and Quinoline.—Chromatography gave quinoline and from an orange band eluted with chloroform 4-*dicyanomethylene*-1,4-*dihydro*-1-(cis-2-*methoxycarbonylvinyl*)*quinoline* (50) (0·3%) as yellow crystals (from chloroform), m.p. 225—228°, *m/e* 278 (19%), 277 (M^+, 100), 246 (28), 219 (10), 218 (44), 217 (23), 191 (10), 165 (14), and 138 (10), m^* 218 (277 ⟶ 246), and 171·5 (277 ⟶ 218).

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