Addition Reactions of Heterocyclic Compounds. Part 68.[1] The Conversion of 1,6-Dihydropyridines into Benzene Derivatives with Dimethyl Acetylenedicarboxylate

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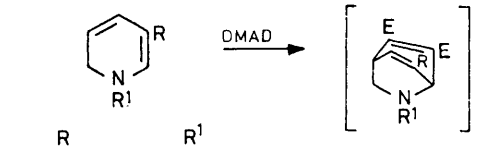
3-Carbamoyl- and 3-cyano-1-methyl-1,6-dihydropyridine, and the 3-carbamoyl-1-benzyl- and -1-phenyl-analogues, with dimethyl acetylenedicarboxylate undergo successive Diels–Alder addition and retrogression giving the corresponding dimethyl phthalates. Other enamine-type additions to the acetylene, and displacement of the carbamoyl group by a *cis*-(1,2-bismethoxycarbonylvinyl) group, occur with these 1,6- and also 1,2- and 1,4-dihydropyridines. The structures of the adducts were deduced mainly from their ^{1}H n.m.r. spectra.

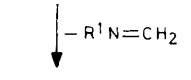
EARLIER investigations concerning reactions between dihydropyridines and dimethyl acetylenedicarboxylate (DMAD) have shown that some 1,2-dihydropyridines behave as enamines giving initially cyclobuta[*b*]pyridines which ring open to azocines,[2,3] while a number of 1,4-dihydropyridines yield stable cyclobuta[*b*]pyridines which do not ring open.[4] In contrast, 1-methyl-1,4-dihydroquinoline with DMAD gives a benzo[*b*]azocine *via* a cyclobutane intermediate.[5] The present paper describes the results of treating further dihydropyridines with DMAD, and different reactions to those previously encountered have been found.

Contrary to what has often been claimed, individual dihydropyridines can be extremely difficult to obtain pure by the reduction of pyridinium salts,[6] and most of the reactions described here were done with mixtures whose composition was known from their ^{1}H n.m.r. spectra. By employing mixtures containing different ratios of dihydropyridines, obtained from the one pyridinium salt using different reducing agents, it was possible to identify the sources of the products.



R	R^1
(1) CN	Me
(2) $CONH_2$	Me
(3) $CONH_2$	Ph
(4) $CONH_2$	$PhCH_2$
(5) E	$PhCH_2$

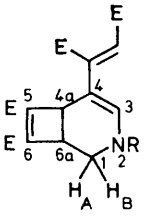
(6)



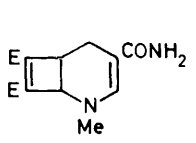
E = CO_2Me

(7) R = CN
(8) R = $CONH_2$
(9) R = CO_2H
(10) R = E

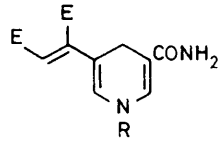
3-Cyano-1-methyl-1,6-dihydropyridine (1) with DMAD in refluxing acetonitrile gives dimethyl 3-cyanophthalate (7). The conversion is thought to proceed *via* a Diels–Alder addition, as occurs with some other 1,2-dihydropyridines with activated olefins,[7] leading to (6), followed by aromatisation through a retro-Diels–Alder reaction. Dimethyl 3-cyano-1-methyl-1,2-dihydroazocine-6,7-dicarboxylate [3] and a cyclobuta[*b*]pyridine [4] derived respectively from the 1,2- and 1,4-dihydro isomers of (1) and present with it were also isolated.



(11) R = Me
(12) R = Ph



(13)



(14) R = Me
(15) R = Ph
(16) R = $PhCH_2$

3-Carbamoyl-1-methyl-1,6-dihydropyridine (2) with DMAD also gave the corresponding phthalic acid derivative (8) identified by conversion into the known (9) with nitrous acid. A second product was the cyclobuta[*c*]pyridine (11). The 4,5-double bond of (2) must possess vinylogous enaminic character, to form the four-membered ring, and subsequent electrophilic attack (*vide infra*) by another acetylene molecule at position 3 followed by amide elimination [4] leads to structure (11). In a similar way 3-carbamoyl-1,6-dihydro-1-phenyl- (3) and -1-benzyl-pyridine (4) gave (8), and dimethyl anilino- and benzylamino-fumarate respectively. These fumarates could have been formed from the amine, arising from hydrolysis of the *N*-methyleneamine produced in the retro-Diels–Alder reaction, combining with DMAD. Also isolated from (3) was dimethyl fumarate and the cyclobuta[*c*]pyridine (12), and in addition the amide (15) which was derived from the 1,4-dihydro isomer of (3) which was present. The possibility that *N*-methylenebenzylamine could be reduced to *N*-methylbenzylamine, because DMAD is reduced to dimethyl fumarate in the reaction mixture, can be discounted. No trace of dimethyl *N*-benzyl-*N*-methylaminomaleate, formed from this amine and DMAD under the conditions of the reaction, could be detected. Compound (4) also gave (16), presumably formed from some 1-benzyl-3-carbamoyl-1,4-dihydropyridine present in the

sample of (4) employed. This is particularly interesting as under other conditions this 1,4-dihydropyridine (4) yields 32% of dimethyl 1-benzyl-3-(*cis*-1,2-bismethoxycarbonylvinyl)-1,4,4a,6a-tetrahydrocyclobuta[*b*]pyridine-5,6-dicarboxylate.[4] The structures of (11) and (12) were deduced mainly from their ^{1}H n.m.r. spectra which were investigated in some detail (Table) and compared with those of other cyclobutapyridines.[4] Reduction of the 1-benzyl-3-methoxycarbonylpyridinium cation as described[8] gave a product containing mainly the 1,6-dihydropyridine (5) which was treated with DMAD. Distillation of the chromatographed product gave trimethyl benzene-1,2,4-tricarboxylate (10), formed *via* (6),

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

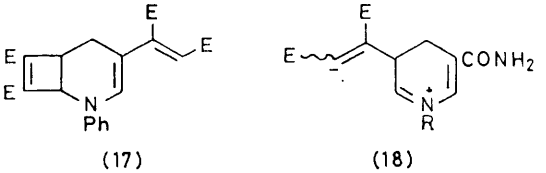
Compound	Proton resonances	Ester Me
(7)	3-H, 2.00;[a] 5,6-H_2, 2.25[a]	6.12, 6.12
(8)	3-H, 1.74d, $J_{3,5}$ 1.5; 5-H, 1.90dd, $J_{5,6}$ 8.5; 6-H, 2.30d	6.13, 6.13
(10)	3-H, 1.58d, $J_{3,5}$ 1.5; 5-H, 1.80dd, $J_{5,6}$ 8.5; 6-H, 2.25d	6.02—6.1 (3 × Me)
(11)[b,c]	2-Me, 7.10; 3-H, 3.62; 4a-H, 6.18d, $J_{4a,6a}$ 4.9; 6a-H, 6.52t, $J_{1A,6a}$ 4.9; 1-H_A, 6.61d, $J_{1A,1B}$ 12.3; 1-H_B, 7.00q; side-chain-H, 4.34	6.13, 6.23, 6.26, 6.33
(12)[b,d]	4′-H, 2.93t; 3′-H, 5′-H, 2.74t; 2′-H, 6′-H, 3.09d; J_{ortho} 7; 3-H, 3.20; 4a-H, 6.11d; $J_{4a,6a}$ 4.6; 1-H_A 6.00d; $J_{1A,1B}$ 12.5; 1-H_B, 6.67dd, $J_{1B,6a}$ 4.5; side-chain-H, 4.11	6.19, 6.28, 6.35, 6.35
(13)	1-Me, 6.93; 2-H, 2.83;[a] 3-$CONH_2$, 4.40;[e,f] 4-H_2, 7.4—7.7m;[g] 4a-H, 6.25—6.5m;[h] 6a-H, 5.85d;[i] $J_{4a,6a}$ 4.7	6.25, 6.25
(14)[j]	1-Me, 6.90; 2-H, 3.05;[a] 3-$CONH_2$, 3.5;[e] 4-H_2, 6.7;[a,e] 6-H, 3.86;[a] side-chain-H, 4.57	6.13, 6.32
(15)	1-Ph and 2-H, 2.45—3.10m; 3-$CONH_2$, 4.00;[e] 4-H_2, 6.83; 6-H, 3.40; side-chain-H, 4.48	6.17, 6.35
(16)	1-$C_6H_5CH_2$, 2.74; 1-$C_6H_5CH_2$, 5.63; 2-H, 2.95; 3-$CONH_2$, 3.82;[f] 4-H_2, 6.92; 6-H, *ca.* 3.8[k]	6.25, 6.38
(17)[l]	1-Ph and 2-H, 2.45—3.4m; 4-H_2 7.2—7.8m; 4a-H, 6.25m; 6a-H, 5.18d;[g] $J_{4a,6a}$ 5; side-chain-H, 4.45	6.18, 6.24, 6.35, 6.35
(A)[m]	Ph 2.72s; $PhCH_2$, 5.50d, $J_{CH_2,NH}$ 6; NH, 1.62br; vinyl-H, 4.87	6.30, 6.40
(B)[m]	Ph, 2.73s; $PhCH_2$, 5.75; Me, 7.28; vinyl-H, 5.45s	6.12, 6.34

[a] Shows signs of splitting. [b] Measured at 270 MHz. [c] Simulated spectrum for the 1-H_A, 1-H_B, 4a, and 6a protons using the parameters given matched the observed spectrum. [d] Primed numbers refer to phenyl proton resonances; the 6a-H resonance is completely hidden under OCH_3 resonances. [e] Broad. [f] Exchanges completely in 30 min with D_2O. [g] Irradiation of 4a-H causes collapse to broad singlet. [h] Simplifies on irradiation of 4-H_2. [i] Collapses to a singlet on irradiation of 4a-H. [j] Solvent $CDCl_3$–CD_3OD–$(CD_3)_2SO$. [k] Obscured by $CONH_2$ resonance. [l] Structure deduced from similarity to 1-benzyl analogue (ref. 4). [m] (A) = Dimethyl *N*-benzylaminofumarate. (B) = Dimethyl *N*-benzyl-*N*-methylaminomaleate.

as the only volatile material. High-pressure liquid chromatography of the reaction mixture gave (10), the azepine and cyclobuta[*b*]pyridine corresponding to the 1,2- and 1,4-isomers of (5), and 1-benzyl-3-methoxycarbonyl-1,2,5,6-tetrahydropyridine also present in the sample of (5), which were obtained as oils and identified only from their ^{1}H n.m.r. spectra.

These results suggest that the enaminic character of the 2,3-double bonds of (1)—(5) is somewhat reduced by resonance interaction with the 3-substituent, in comparison with the corresponding 1,2-dihydropyridines, encouraging Diels–Alder additions at the expense of electrophilic attack by the acetylene on the enaminic system. This is consistent with Büchi's explanation and observations that while he was able to isolate Diels–Alder adducts from 1,6-dihydropyridines [*e.g.* (5)] with methyl acrylate none arising from the isomeric 1,2-dihydropyridines were ever observed.[8]

The reaction of 3-carbamoyl-1-methyl-1,4-dihydropyridine with DMAD is particularly interesting as it affords the amide (13), along with the much less basic (14); the related formation of the amide (16) has already been mentioned. In all similar cases examined displacement of the amide group occurs, for example in the formation of (11) and (12). This suggests, in agreement with the expected electronic effect of the 3-carbamoyl group, that the cyclobutane ring is formed before a second electrophilic attack by DMAD leads to amide elimination. 3-Carbamoyl-1-phenyl-1,4-dihydropyridine similarly gives (15), along with (1). The u.v. spectra of (12) and (17) differ only in the extinction coefficients (ε 27 700 and 13 200 respectively) of the long wavelength band (*ca.* 327 nm) and this can be associated with the greater steric hindrance to conjugation of the phenyl group with the enaminic system in (17). The isolation of (14) and (15) supports the usual supposition that the formation of the cyclobutane ring is not a concerted process and that the expected zwitterionic intermediate (18) can either cyclise or accept a proton. Compound (15) was recovered unchanged after being heated in refluxing benzene or diphenyl ether, and after irradiation in methanol



(17) (18)

ECH=ĊE

(19)

The mass spectra of the bicyclic adducts (11) and (12) are similar (M^+, 20 and 39% respectively) and show a series of losses of methoxy, ester, and related fragments. In addition both show the loss of masses corresponding to DMAD (23 and 18%) and to (19) (100 and 60%), and compound (11) also shows positive ions corresponding to these fragments (22 and 17% respectively). Compound (17) has similar ester-group derived fragmentations, the loss of (19) (14%), while the base peak is at *m/e* 77 (C_6H_5). The bicyclic amide (13) fits into this pattern, the molecular ion (50%) losing fragments corresponding to CO_2Me (36%), DMAD (21%), and (19) (100%). In contrast to (14) and (15), (13) showed a significant loss

of $CONH_2$ (28%), but no loss of a hydrogen atom or a methyl fragment, from the molecular ion. Compounds (11), (12), (14), (15), (16), and (17) all yielded a fragment (43, 30, 100, 10, and 24% respectively) corresponding to the loss of two ester groups and one hydrogen atom, and this may be associated with the 1,2-bismethoxycarbonyl side-chain as a corresponding loss is not shown by (13); the base peak for (16) corresponds to $C_7H_7^+$.

No losses corresponding to DMAD or (19) from (14) or (15) could be detected. This last type of fragmentation can be associated with the presence of the cyclobutapyridine ring in our compounds, and also takes place for all the *N*-benzyl derivatives with the ring system of (13) described earlier [4] with the exception of dimethyl 1-benzyl-3-(*N*-ethyl-*N*-phenylcarbamoyl)-1,4,4a,6a-tetrahydrocyclobuta[*b*]pyridine-5,6-dicarboxylate when loss of PhEtN gave a very stable base peak. However, even in this case reduction to the 5,6-dihydro-derivative diminished the effect of the *N*-ethylanilino-group for although its loss gave rise to the base peak the molecular ion also lost the elements of dimethyl fumarate, which now corresponds to the loss of DMAD in the earlier cases mentioned.

EXPERIMENTAL

The instruments used, deactivated alumina used for chromatography (unless otherwise stated), and general procedures are described in earlier papers in this series. The reduced pyridines were prepared as reported unless otherwise stated. All analyses for new compounds were within accepted limits for C, H, and N, and along with the i.r., u.v., and mass spectra are available as Supplementary Publication No. SUP 22385 (6 pp.).*

3-Cyano-1-methyl-1,6-dihydropyridine with Dimethyl Acetylenedicarboxylate.—(i) The ester (5.7 g), a mixture of 1,2- and 1,6-dihydro-3-cyano-1-methylpyridine (4.6 g; 2 : 1 ratio by n.m.r.), prepared as described,[9] and acetonitrile (40 ml) were heated under reflux for 17 h and then evaporated. The residue in dichloromethane was chromatographed over alumina and the material eluted with ether was rechromatographed from dichloromethane over silica. Elution with ether gave dimethyl 4-cyanophthalate (7) (1.1 g), b.p. 115—125 °C at 0.02 Torr, *m/e* 219 (M^+), followed by an orange oil (3.4 g) yielding dimethyl 3-cyano-1-methyl,1,2-dihydroazocine-6,7-dicarboxylate identical with an authentic specimen.[3]

The cyanophthalate (0.42 g) in chloroform (3 ml) and dry methanol (2 ml) was saturated at 0—5 °C with hydrogen chloride, and after 63 h at 25 °C the solvent was evaporated off. The residue, in ether, was washed with aqueous sodium hydrogen carbonate, dried, and rechromatographed to give trimethyl benzene-1,2,4-tricarboxylate (10) (0.3 g) as an oil which solidified completely at −20 °C and had m.p. −10 to −14 °C (lit.,[10] −13 °C).

(ii) The ester (2.9 g) and a mixture of 1,4- and 1,6-dihydro-3-cyano-1-methylpyridine (2.3 g; 1 : 1 ratio) in acetonitrile were heated under reflux for 12 h. Chromatography failed to resolve the resulting mixture but distillation gave dimethyl 4-cyanophthalate, b.p. 140—150 °C at 0.25—0.4 Torr, identical in spectra to the sample from (i), and the residue after purification gave dimethyl 3-cyano-1-methyl-1,4,4a,6a-tetrahydrocyclobuta[*b*]pyridine-5,6-dicarboxylate identical with an authentic specimen.[4]

3-Carbamoyl-1-methyl-1,4-dihydropyridine with Dimethyl Acetylenedicarboxylate.—The ester (4 ml) and the 1,4-dihydropyridine [6] (3.94 g, containing 10% of the 1,6-isomer) in benzene (30 ml) and acetonitrile (30 ml) were heated under reflux for 15 h, evaporated, and the product dissolved in dichloromethane. Chromatography and elution with benzene–dichloromethane (4 : 1, v/v) gave first dimethyl fumarate (0.22 g), followed by dimethyl 3-carbamoyl-1-methyl-1,4,4a,6a-tetrahydrocyclobuta[*b*]-pyridine-5,6-dicarboxylate (13) (1.40 g), orange prisms (from ether), m.p. 163—165 °C.

In a similar reaction the dichloromethane solution was extracted with 1M hydrochloric acid; the aqueous solution on basification and re-extraction (CH_2Cl_2) yielded (13) (0.73 g) after silica column chromatography. Chromatography of the non-aqueous phase (over alumina) gave 5-(cis-1,2-*bismethoxycarbonylvinyl*)-3-*carbamoyl*-1-*methyl*-1,4-*dihydropyridine* (14), yellow-orange prisms (from benzene–chloroform–ether), m.p. 174—176 °C. Only (13) (0.95 g), extracted by 1M hydrochloric acid, was isolable from a similar reaction in acetonitrile (20 °C; 13 days).

3-Carbamoyl-1-methyl-1,6-dihydropyridine with Dimethyl Acetylenedicarboxylate.—The ester (1 ml) and a mixture of the 1,4- and 1,6-dihydro-3-carbamoyl-1-methylpyridine (1 g; 1 : 1 ratio) [6] in acetonitrile (50 ml) were heated under reflux for 22 h, and then evaporated, and the dichloromethane–benzene (1 : 10) soluble fraction of the residue chromatographed. Elution with benzene gave an oil (150 mg) which yielded dimethyl 4-(*cis*-1,2-bismethoxycarbonylvinyl)-2-methyl-1,2,4a,6a-tetrahydrocyclobuta[*c*]-pyridine-5,6-dicarboxylate (11), yellow prisms (from ether), m.p. 139—141 °C. Elution with benzene–ethanol (9 : 1, v/v) gave a mixture of dimethyl 4-carbamoylphthalate (8), m.p. 123—125 °C, and the cyclobuta[*b*]pyridine (13) identical with an authentic specimen. The mixture was separated by fractional crystallisation from methanol–water, the phthalate being the less soluble, and also by extraction with 1M aqueous hydrochloric acid in which only the pyridine dissolved.

The carbamoylphthalate (8) (0.1 g) dissolved in conc. sulphuric acid (1 ml) was diluted with a little water and treated with excess of sodium nitrite. Next day the precipitated 3,4-dimethoxycarbonylbenzoic acid (9) was recrystallised (benzene–ether) as prisms which had m.p. 111.5—117 °C, resolidifying and remelting at 121 °C in agreement with the literature.[10]

3-Carbamoyl-1-phenyl-1,4-dihydropyridine with Dimethyl Acetylenedicarboxylate.—(i) The pyridine (1.35 g) and the ester (1 g) were heated under reflux in chloroform (25 ml) for 21 h; essentially the same result was obtained using acetonitrile at 20 °C for 9 days. Evaporation and chromatography gave 5-(*cis*-1,2-bismethoxycarbonylvinyl)-1-phenyl-1,4-dihydropyridine-3-carboxamide (15) (750 mg), yellow prisms (from methanol), m.p. 172—174 °C.

(ii) Heating the pyridine (2 g) with the ester (2.8 g) under reflux in dry benzene (50 ml) for 9 h, chromatography, and elution with benzene gave *dimethyl* 3-(cis-*bismethoxycarbonylvinyl*)-1-*phenyl*-1,4,4a,6a-*tetrahydrocyclobuta*[b]*pyridine*-5,6-*dicarboxylate* (17) (210 mg), yellow prisms (from methanol), m.p. 173—174 °C. Elution with ether then gave an orange band yielding an unidentified 1 : 1 molar adduct, yellow prisms (from methanol), m.p. 180—

* For details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

182 °C, *m/e* 342 (*M*) and more polar solvents eluted the pyridine (15) (0.7 g).

3-Carbamoyl-1-phenyl-1,6-dihydropyridine with Dimethyl Acetylenedicarboxylate.—The ester (1.6 g), the pyridine [6] (3) (2 g), chloroform (30 ml), and acetonitrile (15 ml) were heated under reflux for 15 h, most of the solvent was removed, and the residue chromatographed on a dry column. Elution with ether gave a mixture of dimethyl fumarate and dimethyl anilinofumarate (0.19 g), followed by dimethyl 4-(*cis*-bismethoxycarbonylvinyl)-2-phenyl-1,2,4a,6a-tetrahydrocyclobuta[*c*]pyridine-5,6-dicarboxylate (12), yellow needles (0.1 g) (from methanol), m.p. 171—172 °C. Elution with methanol and rechromatography of the eluate using ether over a dry silica gel (100—200 mesh) column gave dimethyl 4-carbamoylphthalate (8) (0.3 g), identical with the previous sample. When the dihydropyridine employed contained the 1,2-dihydro-isomer, dimethyl 3-carbamoyl-1-phenyl-1,2-dihydroazocine-6,7-dicarboxylate was isolated in addition to the products just described.

1-Benzyl-3-methoxycarbonyl-1,6-dihydropyridine (5) *with Dimethyl Acetylenedicarboxylate.*—The pyridine (5) (11.9 g) prepared as described [8] and dimethyl acetylenedicarboxylate (6.5 ml) were stirred in acetonitrile (60 ml) for 31 h at room temperature, and the solvent was removed to give an oil (19 g). Chromatography (of 1 g) over silica (80—200 mesh) and elution with toluene gave a mixture from which trimethyl benzene-1,2,4-tricarboxylate (10) (0.18 g), b.p. 125—130 °C (bath) at 0.4 Torr, was isolated, and which was identical in spectra with the previously described specimen.

1-Benzyl-3-carbamoyl-1,6-dihydropyridine (4) *with Dimethyl Acetylenedicarboxylate.*—The ester (2.7 ml) in acetonitrile (50 ml) was heated under reflux for 22 h with (4) (4.42 g) prepared as described [8] but which was a mixture (determined by n.m.r.) of (4) with the 1,4-dihydro-isomer and the 1,2,5,6-tetrahydropyridine in a 1 : 1 : 0.5 ratio respectively. After removal of solvent, chromatography of the residue over alumina and elution with dichloromethane–ether followed by chloroform gave three main fractions, which were rechromatographed, to give (a) dimethyl benzylaminofumarate (200 mg), identical in b.p. and spectral properties to authentic material described later; (b) after an initial extraction with 6M hydrochloric acid to remove basic materials, the *dihydropyridine* (16) (300 mg), yellow prisms, m.p. 147—150 °C (from aqueous methanol); (c) the amide (8) (0.89 g).

Dimethyl N-Benzylaminofumarate.—Dimethyl acetylenedicarboxylate (6.5 ml) was added to benzylamine (5.35 g) in ether (100 ml) when some heat was evolved. Next day distillation gave dimethyl *N*-benzylaminofumarate (9.0 g), b.p. 110—115 °C at 0.2—0.3 Torr; $\lambda_{max.}$ (MeOH) 211 (ε 9 864) and 312 (12 016) nm; $\nu_{max.}$ (film) 3 300s, 1 740s, 1 670s, and 1 610s cm^{-1}.

Dimethyl N-Benzyl-N-methylaminomaleate.—Dimethyl acetylenedicarboxylate (7.1 g) and benzylmethylamine (10 g) were treated as just described, or in acetonitrile at room temperature or under reflux, but the syrup obtained on solvent removal crystallised to give *dimethyl N-benzyl-N-methylmaleate* as white leaflets (10.7 g) (from MeOH), m.p. 72—73 °C; $\lambda_{max.}$ (MeOH) 210 (ε 9 606) and 285 (25 770) nm; $\nu_{max.}$ (Nujol) 1 740s, 1 695s, 1 590m, and 1 570s cm^{-1}.

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