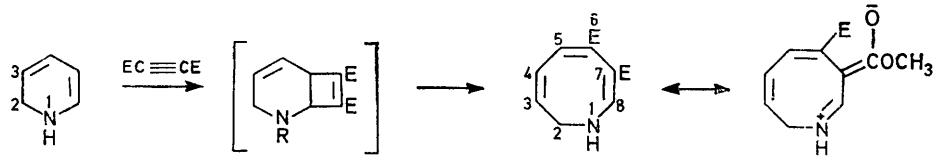
Addition Reactions of Heterocyclic Compounds. Part LVI.[1] Formation of 1,2-Dihydroazocines from 1,2-Dihydropyridines with Dimethyl Acetylenedicarboxylate

By **R. Morrin Acheson,* Giuseppe Paglietti,** and (in part) **Peter A. Tasker,** Department of Biochemistry, South Parks Road, Oxford OX1 3QU

1-Phenyl- (1), 1-phenyl-3-carbamoyl- (2), 1-methyl-3-cyano- (3), and 1-benzyl-4-methyl-1,2-dihydropyridine (4) with dimethyl acetylenedicarboxylate gave the corresponding dimethyl 1,2-dihydroazocine-6,7-dicarboxylates, a 1,2,4a,6a-tetrahydrocyclobuta[*b*]pyridine being detected as an intermediate in one case. N.m.r. variable temperature spectra gave evidence of ring flipping in the azocines but showed no valence tautomerism. The 3,4- and 5,6-double bonds of the azocines were reduced respectively by hydrogen over palladium and by sodium borohydride. Photolysis cyclised dimethyl 1,2-dihydro-1-phenylazocine-6,7-dicarboxylate (6) across the 3,6-positions to give the 1,2,4a,6a-tetrahydrocyclobuta[*c*]pyridine (17).

RECENTLY we have described [2] the formation of stable cyclobutapyridines from 1,4-dihydropyridines with dimethyl acetylenedicarboxylate, and although the four-membered rings of these compounds have not been opened, the corresponding cyclobutene from 1-methyl-1,4-dihydroquinoline has been detected as an intermediate and found to open rapidly to give dimethyl 1-methyl-1,6-dihydrobenzo[*b*]azocine-3,4-dicarboxylate.[3]



(1) 1 - Ph
(2) 1 - Ph, 3 - $CONH_2$
(3) 1 - Me, 3 - CN
(4) 1 - CH_2Ph, 4 - Me

(5)

(6) 1 - Ph
(7) 1 - Ph, 3 - $CONH_2$
(8) 1 - Me, 3 - CN
(9) 1 - CH_2Ph, 4 - Me

E = CO_2Me throughout

N-Substituted 1,2-dihydropyridines could behave as butadienes, or like their 1,4-dihydro-analogues as enamines, towards αβ-unsaturated carbonyl compounds

[1] Part LV, R. M. Acheson and M. S. Verlander, *J.C.S. Perkin I*, 1974, 430.

[2] R. M. Acheson, N. D. Wright, and P. A. Tasker, *J.C.S. Perkin I*, 1972, 2918.

[3] P. G. Lehman, *Tetrahedron Letters*, 1972, 4863.

and few reactions in this general area have been examined.[4] *N*-Phenyl-[5] and *N*-methoxycarbonyl-1,2-dihydropyridine[6] with *N*-phenylmaleimide and maleic anhydride respectively yield Diels–Alder type adducts, while 3-cyano-1-methyl-1,6-dihydropyridine with acrylonitrile yields a structurally similar adduct.[7] Analogy suggested that 1,2-dihydropyridines could react with acetylenic esters in a number of ways, and the present investigation[8] was designed to examine these reactions.

TABLE 1

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

Compound	Recording frequency (MHz)	Proton resonances	Ester methyl groups
(6)	60, 100,[a] 220	1-Ph, 2·5—3·0 m; 2-H_2, 5·5br d; 3-H, 3·66 dt; 4-H, 3·41 dd; 5-H, 3·18 d; 8-H, 2·12; $J_{2,3}$ 7; $J_{3,4}$ 10; $J_{4,5}$ 3	6·30, 6·43
(7)	60	1-Ph, 2·6—3·0 m; 2-H_2, 5·10 s; 3-$CONH_2$, 3·83;[b] 4-H, 2·71 d;[c] 5-H, 3·12 d;[c] 8-H, 2·10; $J_{4,5}$ 4	6·27, 6·43
(8)	60, 90	1-Me, 6·93; 2-H_2, 5·73;[d] 4-H, 2·72d;[e] 5-H, 3·38;[e] 8-H, 2·50; $J_{4,5}$ 4	6·30, 6·45
(9)	60	1-Ph, 2·75 m; 1-PhCH_2, 5·80 s; 2-H_A, *ca.* 5·7br 2-H_B, 6·8br; 3-H, 4·35 t;[e] 4-Me, 8·20; 5-H, 3·45; 8-H, 2·30; $J_{2,3}$ 8	6·28, 6·42
(10)	60	1-Ph, 2·5—3·2 m; 2-H_2, 5·5;[d] 3,4,5-H_3, 3·2—4·0 m;[f] 6-CO_2H, 3·1;[g] 8-H, 2·06	6·43
(11)	60	1-*Ph*CH_2, 2·5—3·0 m; 1-PhCH_2, 5·75; 2-H_A, *ca.* 5·5;[h] 2-H_B, *ca.* 6·9;[h] 3-H, 4·35 t;[e] 4-Me, 8·20; 5-H, 3·35; 6-COOH, 1·4;[g] 8-H, 2·28; $J_{2,3}$ 8	6·40
(12)	60[i]	1-Ph, 2·5—3·2 m; 2-H_2, 5·80 dq; 3-H_2, 8·0—9·0 m; 4-H_2, 7·55 m; 5-H, 3·55 t; 8-H, 2·18; $J_{4,5}$ 8·3	6·28, 6·39
(13)	60	1-Ph, 2·5—3·1 m; 2-H_2, 5·8 m; 3-H_2, 8·0—9·0 m; 4-H_2, 7·55 m; 5-H, 3·40 t; 6-CO_2H;[j] 8-H, 2·16; $J_{4,5}$ 8	6·35
(14)	60[k]	1-Ph, 2·6—3·0 m; 2-H_2, 3-H, 5·8—6·3 m; 4-H_2, 7·5 m; 5-H, 3·6;[l] 8-H, 2·32	6·30, 6·40
(15)	60,[m] 90,[m] 270	1-Ph, 2·5—3·1 m; 2-H_A, 5·44 q; 2-H_B, 6·00 q; 3,4-H_2, 3·9—4·65 m; 5-H_2, 7·15 m; 6-H, 5·57 t 8-H, 2·04; $J_{2A,2B}$ 16; $J_{2A,3}$ = $J_{2B,3}$ 8; $J_{5,6}$ 7	6·37, 6·40
(16)	60	1-Ph, 2·5—3·1 m; 2-H_2, 5·8—6·4 m;[n] 3,4,5-H_3, 7·5—8·5 m; 6-H, 5·60 t; 8-H, 2·04; $J_{5,6}$ 7	6·32, 6·34
(17)	270	1-H_A, 6·395 d; 1-H_B, 6·512 q; 2-Ph, 2·6—3·0 m; 3-H, 2·25; 5-H, 3·76 d;[e] 6-H, 3·73 d;[e] 6a-H, 6·585; $J_{1\text{-}HA,1\text{-}HB}$ 9·8; $J_{1\text{-}HB,6a}$ 2·6; $J_{5,6}$ *ca.* 2·5	6·26, 6·30
(18)	100, 270[o]	1-H_2, 6·5—6·6 m; 2-Ph, 2·5—3·0 m; 3-H, 1·90; 5,6,6a-H_3, 6·8—7·2 m; 8·0—8·4 m	6·30, 6·30

[a] Irradiation of 2-H_2 collapsed 3-H to d. Irradiation of 5-H collapsed 4-H to d, and of 4-H showed coupling with 3- and 5-H. [b] Broad s exchanges with D_2O. [c] These resonances could be interchanged. [d] Broad s. [e] 2 Hz additional coupling with 4-Me proved by double resonance; irradiation of 2-H_A or 2-H_B also caused simplification. [f] Identical with the 60 MHz spectrum of (6) for these protons. [g] Exchanged with D_2O. [h] Very broad; irradiation simplifies 3-H, and irradiating 3-H simplifies this resonance. [i] Irradiation at 3·55 simplified the 7·55 multiplet, and irradiation at 7·55 collapsed the 5-H t to s. Irradiation of 3-H_2 changes the 7·55 resonance to d and simplifies the 2-H_2 resonance. [j] Not observed. [k] In $(CD_3)_2SO$. [l] Almost t $J \simeq J \simeq 8$. Irradiation of 4-H_2 collapsed this to s and simplified the 5·8—6·3 m. [m] Irradiation of 3,4-H_2 collapsed 5-H_2 to an approximate d and simplified the 2-H_2 resonance to q. Irradiation of 6-H simplified the 5-H_2 to a broad s. Irradiation of 5-H_2 collapsed the 6-H to a broad s. [n] Partially obscured by OMe resonances. [o] Aliphatic resonances not assignable at this frequency.

The 1,2-dihydropyridines (1)—(4) with dimethyl acetylenedicarboxylate in ether or acetonitrile gave good yields of the azocines (6)—(9), which are probably formed through the intermediacy of cyclobutapyridines,[2,3] but (1) did not give crystalline products with methyl propiolate or phenylpropiolate.

Evidence for the intermediacy of the cyclobutene (5; R = Ph) was obtained by mixing the dihydropyridine (1) with dimethyl acetylenedicarboxylate in deuteriochloroform at *ca.* −50° and observing the n.m.r. spectrum at successively increasing temperatures. The superimposed spectra of (1) and the ester were observed at −50°, and between −10 and 0° the doublet due to the 2-protons of (1) completely disappeared while a multiplet appeared at τ 3·4—4·2, a doublet at 4·85 (J *ca.* 4 Hz) and a quartet at 5·35. These new resonances are assigned to the 3,4-olefinic protons, and the 6a- and 4a-protons respectively of the cyclobutene (5). Re-examination after warming to 20° showed that these three resonances had disappeared and had been replaced by a low field singlet (τ 2·08) which was just detectable in the −10° spectrum, and resonances at τ 3·3—3·9 and 5·5 characteristic of the azocine 8-, 3,4,5-, and 2-protons respectively.[4]

The azocines (6)—(8) showed similar n.m.r. spectra, that of (6) being examined in detail (Table 1), the relationships between all the coupled protons being confirmed by double resonance experiments. At 35° the methylene groups of (6)—(8) appeared as a doublet, and sharp and broad singlets respectively, but lowering the temperature (Table 2) caused reversible non-equivalence to occur, the changes being complete

TABLE 2

Variable temperature n.m.r. spectra (τ values; J in Hz) measured at 90 MHz in deuteriochloroform using internal tetramethylsilane as reference

Compound	Temp. (°C)[a]	Variations from 35° spectra
(6)[b]	−40	2-H_A, 4·83 q;[c] 2-H_B, 6·07 q;[c] $J_{2\text{-}H_A,2\text{-}H_B}$ 14; $J_{2\text{-}H_A,3}$ 8; $J_{2\text{-}H_B,3}$ 5·5
(7)	−20	2-H_2 split into two broad peaks,[d] *ca.* 4·9 and 5·2
(8)[e]	−20	2-H_A, 4·81;[f] 2-H_B, 6·51;[f] $J_{2\text{-}H_A,2\text{-}H_B}$ 14
(9)	+10	2-H_A, 5·45 dd; 2-H_B 6·90 dd; $J_{2\text{-}H_A,2\text{-}H_B}$ 14; $J_{2\text{-}H_A,3}$ 8·5; $J_{2\text{-}H_B,3}$ 6·5
(15)	−50	6-H, 5·47 q;[g] J 6 and 9·5

[a] Temperature at which complete change was observed. [b] Solvent CS_2. [c] Coalescence at *ca.* −10°. [d] Coalescence *ca.* 5°. [e] Also at 60 MHz. [f] Coalescence at *ca.* 10°. [g] At −20° this q is a t, J 8 and 8.

[4] U. Eisner and J. Kuthan, *Chem. Rev.*, 1972, **72**, 1.
[5] M. Saunders and E. H. Gold, *J. Org. Chem.*, 1962, **27**, 1439.
[6] F. W. Fowler, *J. Org. Chem.*, 1972, **37**, 1321.
[7] K. Schenker and J. Druey, *Helv. Chim. Acta*, 1962, **45**, 1344.
[8] R. M. Acheson and G. Paglietti, *J.C.S. Chem. Comm.*, 1973, 665.

by or before −40°; the rest of the spectra were little changed. This shows that the 8-membered ring is quite flexible and that flipping stops at lower temperatures The azocine (9) was more rigid. No evidence for cyclisation across the 3,6-positions to give an azetidine, corresponding to the cyclo-octa-1,3,5-triene–bicyclo[4.2.0]octa-2,4-diene [9] type of valence tautomerism reported for some fully unsaturated azocines,[10] was found under our conditions.

In contrast the n.m.r. spectrum of 1-phenyl-1,2-dihydropyridine does not change between +35 and −40°. The possibility that the temperature-dependent changes for the azocines (6)—(8) are due to a slowing of nitrogen inversion, rather than ring-flipping, is unlikely because the spectrum of the rigid cyclobutapyridine (17), which possesses the same conjugated system involving nitrogen as compounds (6)—(8), shows only small changes of a different type on reducing the temperature to −50°. The 8-proton for the azocines (6)—(8), and also for all the other azocines (9)—(16) which possess the same grouping where the 3-ester group can deshield the 2-proton, appears at rather low field (τ 2·1). This is expected by analogy with the 3-proton (τ 2·07) of methyl *trans*-3-anilinoacrylate,[11] but is at rather low field compared with the 2-proton of 8-methoxyazocine.[12]

The azocine (6) did not react with *N*-bromosuccinimide, bromine, diazomethane, ammonia, methyl iodide, or with refluxing dimethyl acetylenedicarboxylate. Mild alkaline hydrolysis of (6) and (9) yielded the monoesters (10) and (11), nucleophilic attack at the 7-ester position presumably being discouraged because of resonance interaction with the nitrogen atom; attempted hydrolysis of (6) by hot aqueous sodium hydroxide, or 6N-hydrochloric acid, gave only some aniline. The i.r. spectrum of the azocine (6), closely resembling those of (7)—(9), shows ester-carbonyl absorption at 1736 and 1680 cm^{-1}, corresponding to the 6- and 7-ester groups. The longer wavelength band corresponds to that of methyl 3-di-isopropylaminoacrylate,[13] which is also a vinylogous amide, and it is this absorption which is unchanged on going from the diesters (6) and (9) to the monoesters, thereby establishing the position of hydrolysis. This interpretation is consistent with i.r. and u.v. (Table 3) data for the azocines.

Hydrogenation of the azocines (6), (7), and (10) saturated the least substituted double bond to give the tetrahydroazocines (12)—(14), identified from their spectra. Attempted reduction of (6) with lithium aluminium hydride or sodium dihydrobis-(2-methoxyethoxy)aluminate gave no characterisable products. However, sodium borohydride in methanol reduced the 5,6-double bond by a Michael-type hydride addition to give (15). In contrast, the 2,3-double bond of 1-methyl-1,6-dihydro-1-benzazocine is reduced [14] by this reagent, but in our case resonance participation by the 7-ester group in (6) inhibits the initial proton addition [15] at position 7 required for this type of reduction.

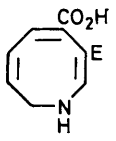
TABLE 3

U.v. spectra in methanol

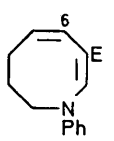
Compound	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$)	
(6)	235 [a] (1·40)	297 (1·90)
(7)	239 (2·21)	304 (2·36)
(8)	243 (2·15)	285 (1·18)
(9)	230 (0·84)	290 (1·52)
(10)	230 (0·91)	300 (1·19)
(11)	235 (0·89)	299 (0·97)
(12)	286 (1·20)	326 (1·46)
(13)	289 infl (1·47)	324 (2·63)
(14)	286 (1·53)	324 (1·79)
(15)	242 infl (0·41)	308 (2·38)
(16)	246 infl (0·23)	307 (3·09)
(17)	236 (0·78)	311 (3·17)
(18)	236 (0·54)	309 (3·39)

[a] Incorrect in ref. 8.

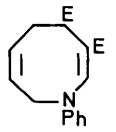
The n.m.r. spectrum of the tetrahydroazocine (15) showed the 6-proton as a triplet at 35° and as a quartet at −50°. The hydrogenation of (15) gave the hexahydroazocine (16).



(10) 1 – Ph
(11) 1 – CH_2Ph,4 – Me

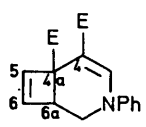


(12) 6 – E
(13) 6 – CO_2H
(14) 3 – $CONH_2$, 6 – E

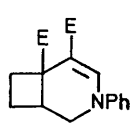


(15)
(16) 3,4 – H_2

Photolysis of the azocine (6) gives the cyclobutapyridine (17), presumably by a concerted disrotatory process, and attempts to reverse the reaction thermally have failed. The structures of (17) and its hydrogenation product (18) follow from their spectra.



(17)



(18)

[9] R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Letters*, 1968, 5215.
[10] L. A. Paquette, T. Kakihana, and J. F. Kelly, *J. Org. Chem.*, 1971, **36**, 435.
[11] R. Huisgen, K. Herbig, A. Seigl, and H. Huber, *Chem. Ber.*, 1966, **99**, 2526.
[12] L. A. Paquette, T. Kakihara, J. F. Hansen, and J. C. Philips, *J. Amer. Chem. Soc.*, 1971, **93**, 152.
[13] R. Huisgen and K. Herbig, *Annalen*, 1965, **688**, 98.
[14] R. M. Coates and E. F. Johnson, *J. Amer. Chem. Soc.*, 1971, **93**, 4016.
[15] 'Enamines—Synthesis, Structure, and Reactions,' ed. A. G. Cook, Dekker, New York, 1969.

The u.v. spectra of compounds (6)—(11) and (15)—(18) are fairly similar (Table 1) and resemble that [11] of methyl (*E*)-3-methyl(phenylamino)acrylate [$\lambda_{max.}$ 220 (10^{-4} ε 0·68) and 297 nm (2·95)]. It appears that the main conjugation in the tub-shaped dihydroazocines is due to the enamine system, and there is little additional conjugation or transannular interaction. In the case of the tetrahydroazocines (12)—(14) models suggest that conformations are possible where the double bonds can be closer to the same plane, which is consistent with the greater conjugation in these compounds.

EXPERIMENTAL

The instruments, deactivated alumina, and general procedures are described in earlier papers in this series. All analyses for new compounds were within accepted limits for C, H, and N, and along with the mass spectra are available as Supplementary Publication No. SUP 21138 (4 pp.).*

Dimethyl 1-*Phenyl*-1,2-*dihydroazocine*-6,7-*dicarboxylate* (6).—1,2-Dihydro-1-phenylpyridine (30 g) and dimethyl acetylenedicarboxylate (30 ml) were refluxed in dry ether (350 ml) for 24 h, and the solution was filtered and evaporated to half volume when the *azocine* (6) (29·1 g) precipitated, as yellow prisms (from ether), m.p. 96—98°, $\nu_{max.}$ 1730s, 1680s, 1615s, and 1592s cm^{-1}. The filtrate from the azocine, on evaporation, chromatography over deactivated alumina, and elution with benzene gave more (8·3 g) azocine.

Dimethyl 3-*Carbamoyl*-1-*phenyl*-1,2-*dihydroazocine*-6,7-*dicarboxylate* (7).—1,2-Dihydro-1-phenylnicotinamide (1·25 g) suspended in dry acetonitrile (20 ml) and dimethyl acetylenedicarboxylate (0·9 ml) at room temperature, gave an orange solution in 1 h. After 4 days the solvent was removed and the residue chromatographed on deactivated alumina. Ether–chloroform–ethanol (50 : 50 : 1, v/v), followed by chloroform, eluted the *azocine* (7), as yellow crystals (1·56 g) (from methanol), m.p. 184—185°, $\nu_{max.}$ 3475, 1720, 1705w, and 1670s cm^{-1}.

Dimethyl 3-*Cyano*-1-*methyl*-1,2-*dihydroazocine*-6,7-*dicarboxylate* (8).—1,2-Dihydro-3-cyano-1-methylpyridine [16] (1·9 g) was treated with dimethyl acetylenedicarboxylate (2·22 g) in dry acetonitrile (10 ml) when the temperature rose rapidly to 50° and the mixture became deep red. After 18 h the solvent was removed, the residue chromatographed, and the *azocine* (8) eluted as an oil (1·69 g) which very slowly formed orange prisms (from ether–light petroleum), m.p. 93—95°, $\nu_{max.}$ 2200w, 1730, 1690, 1615w, and 1585w cm^{-1}.

Dimethyl 1-*Benzyl*-4-*methyl*-1,2-*dihydroazocine*-6,7-*dicarboxylate* (9).—1-Benzyl-1,2-dihydro-4-methylpyridine (0·59 g) was treated with the acetylenic ester (0·42 ml) in acetonitrile (10 ml) and chromatographed, as for (8), to give an oil. Rechromatography over alumina, eluting with ether, gave the *azocine* (9) as an oil, $\nu_{max.}$ 1720s, 1690s, and 1590s cm^{-1}.

Hydrolysis of the Dihydroazocine (6).—(*a*) The azocine (6) (1·5 g) was stirred with 2N-aqueous sodium hydroxide (12 ml) and methanol (15 ml) for 3 days, more methanol was added, and stirring continued for 7 days. The solution was evaporated (45°), diluted with water (10 ml), extracted with ether, and the aqueous layer acidified with 6N-hydrochloric acid (4 ml). 7-*Methoxycarbonyl*-1-*phenyl*-1,2-*dihydroazocine*-6-*carboxylic acid* (10) (0·33 g) precipitated, as yellow prisms (from ethanol), m.p. 166—168° (decomp.), $\nu_{max.}$ 3410s, 2515br, and 1670 cm^{-1}.

(*b*) The azocine (6) (0·94 g) was refluxed under nitrogen with sodium hydroxide (0·64 g) in water (58 ml) for 4 h and cooled. The precipitated oil (130 mg) was collected with ether, refluxed with acetic anhydride (1 ml), and diluted with water (5 ml) when acetanilide (141 mg), identical in m.p., mixed m.p., and i.r. spectrum with an authentic specimen, was obtained.

(*c*) Refluxing (6) (0·94 g) with 6N-aqueous hydrochloric acid (10 ml) and methanol (20 ml) similarly gave aniline.

Hydrolysis of the Dihydroazocine (9).—The azocine (0·58 g), ethanol (5 ml), and 2N-aqueous sodium hydroxide (12 ml) were stirred at room temperature for 4 days when homogeneity was reached. After evaporation, dilution with water, and ether extraction the aqueous solution was acidified. The oil was collected with ether, and evaporation gave the 1-*benzyl*-7-*methoxycarbonyl*-4-*methyl*-1,2-*dihydroazocine*-6-*carboxylic acid* (11) (0·24 g), as yellow prisms (from benzene–pentane), m.p. 154—156°, $\nu_{max.}$ 3200—2400br, 2650, 2540, 1685s, 1620, and 1585s cm^{-1}.

Dimethyl 1-*Phenyl*-1,2,3,4-*tetrahydroazocine*-6,7-*dicarboxylate* (12).—The azocine (6) (3·0 g) in ethanol (25 ml) was added to palladised charcoal (10%; 1 g) suspended in ethanol (20 ml) and previously saturated with hydrogen. After 5 min at room temperature and pressure theoretical absorption for one double bond had occurred, and the solution was filtered and evaporated. The oily residue crystallised from ethanol–water, after 5 days at 0°, to give the *tetrahydroazocine* (12) (2·75 g), m.p. 105—107°, $\nu_{max.}$ 1720m, 1680s, 1615s, and 1590s cm^{-1}.

7-*Methoxycarbonyl*-1-*phenyl*-1,2,3,4-*tetrahydroazocine*-6-*carboxylic Acid* (13).—The dihydroazocine (10) on hydrogenation as for (6), but in methanol, gave the *tetrahydroazocine* (13) (*ca.* 100% yield), as yellow prisms (from aqueous methanol), m.p. 157—158°, $\nu_{max.}$ 2620br, 1685s, 1625w, and 1580s cm^{-1}.

Dimethyl 3-*Carbamoyl*-1-*phenyl*-1,2,3,4-*tetrahydroazocine*-6,7-*dicarboxylate* (14).—The dihydroazocine (7) (0·21 g) was hydrogenated as for (6) but heating to 55° was necessary. The *tetrahydroazocine* was obtained as prisms (from aqueous ethanol), m.p. 190—195°, $\nu_{max.}$ 3435s, 3330w, 3290w, 3230w, 1700, 1695s, 1675w, 1630w, and 1600s cm^{-1}.

Dimethyl 1-*Phenyl*-1,2,5,6-*tetrahydroazocine*-6,7-*dicarboxylate* (15).—Sodium borohydride (3·88 g) in methanol (20 ml) was dropped into the dihydroazocine (6) (1 g) in methanol (10 ml) cooled in ice. After the vigorous evolution of hydrogen subsided the mixture was refluxed for 24 h and most of the methanol evaporated off. The residue was treated with water, extracted with chloroform (3 × 25 ml), and evaporation of the washed and dried (Na_2SO_4) extract gave the *tetrahydroazocine* (15) (0·89 g) as an oil, which crystallised (ether–pentane) with difficulty giving prisms (0·36 g), m.p. 88—88·5°, $\nu_{max.}$ 1735s, 1680s, and 1575s cm^{-1}.

Hydrogenation of (15) (0·3 g) essentially as for (6) gave

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

[16] N. Kinoshita and T. Kawasaki, *Yakugaku Zasshi*, 1963, **83**, 123.

dimethyl 1-*phenyl*-1,2,3,4,5,6-*hexahydroazocine*-6,7-*dicarboxylate* (16) (0·16 g) as crystals (from aqueous ethanol), m.p. 70—72°, $\nu_{max.}$ 1730, 1670, 1612, and 1590 cm^{-1}.

Dimethyl 2-*Phenyl*-1,2,4a,6a-*tetrahydrocyclobuta*[c]*pyridine*-4,4a-*dicarboxylate* (17).—The azocine (6) (1·5 g) was photolysed in methanol (*ca.* 550 ml) using a quartz vessel and a 300 W Hanovia lamp for 1 h. The methanol was evaporated off and the residue, in ether, was treated with pentane at 0°. The *cyclobuta*[c]*pyridine* (17) precipitated, as prisms (0·39 g) (from methanol), m.p. 124—126°, $\nu_{max.}$ 1725, 1690, 1625, and 1595 cm^{-1}.

Hydrogenation of (17) (0·29 g), as for (6), was complete in 8 min and gave *dimethyl* 2-*phenyl*-1,2,4a,5,6,6a-*hexahydrobuta*[c]*pyridine*-4,4a-*dicarboxylate* (18), as prisms (0·14 g) from ether), m.p. 119—121°, $\nu_{max.}$ 1725s, 1680s, 1630s, and 1595s cm^{-1}.

We thank Mrs. E. E. Richards for the 90 and 100 MHz spectra, Dr. I. D. Campbell for the 270 MHz spectra, Mr. P. J. Abbott for the mass spectra, and the S.R.C. for the V.T. probe for our Perkin-Elmer R12 spectrometer. We also thank Dr. J. Feeney for some 100 MHz spectra, Dr. B. Sheard for the 220 MHz spectrum which was measured on a Varian HA 220, made available through an S.R.C. grant, at the I.C.I. Petrochemicals and Polymer Laboratory, and the University of Naples for study leave to G. P.

[4/1363 *Received*, 8*th July*, 1974]