Ring Expansion and Photochemical Ring Contraction Reactions of Tetrahydropyridazinones

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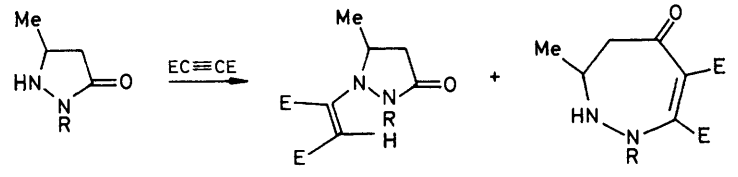
Dimethyl acetylenedicarboxylate reacts with 6-methyl-2-phenyl- and -2-cyclohexyl-tetrahydropyridazin-3-ones (7) and (8) to give 1-anilino- and 1-cyclohexylamino-tetrahydroazepin-4-ones (10) and (11). No maleate ester derivatives, such as the oxopyrazolidinylmaleate (4) formed when 2-benzyl-5-methylpyrazolidin-3-one (2) reacts with the ester, are obtained with the pyridazinones. 6-Methyl-2-phenyltetrahydropyridazin-3-one (7) undergoes photochemical ring contraction to 1-anilino-5-methylpyrrolidin-2-one (12).

THE reactions of pyridazinones and dihydropyridazinones have been widely studied; tetrahydropyridazinones seem to be less well known.[1] In an earlier paper [2] we described the background to our work on the reaction of dimethyl acetylenedicarboxylate, a reagent which has been widely used with a variety of heterocyclic compounds to create novel ring systems, with 2-phenylpyrazolidin-3-ones such as (1) (Scheme 1) to give tetrahydro-1,2-diazepin-5-ones (5). We have now extended our study to the ring transformation reactions of tetrahydropyridazinones (Scheme 2).

Hydrogenation of 4,5-dihydro-6-methyl-2-phenylpyridazin-3(2*H*)-one (6) over platinum in glacial acetic acid at 3 atm led to a mixture from which the tetrahydro- (8) and the dihydro-cyclohexylpyridazinone (9) as well as the desired phenyltetrahydropyridazinone (7) could be isolated by chromatography. The structures of the pyridazinones in which the phenyl ring had been reduced were established by analysis as well as by spectroscopic methods. The reduction of the aromatic ring was shown by the absence of any aromatic proton signals in the ^{1}H n.m.r. spectra. The mass spectrum of the tetrahydropyridazinone (8) shows a base peak (*m/e* 114) corresponding to the loss of cyclohexene with migration of a hydrogen atom to the carbonyl group. For the dihydropyridazinone (9), two fragments of similar importance appear, one, *m/e* 112, corresponding again to the loss of cyclohexene with migration of one hydrogen atom, *m/e* 113, representing a cleavage requiring the abstraction of two hydrogen atoms from the cyclohexane ring (Scheme 3). The unusual reduction of the aromatic ring with survival of the imine function in the dihydropyridazinone (9) was further confirmed by the appearance of the methylene signal of the pyridazinone ring as a singlet at δ 2.3, a feature that appears also in the ^{1}H n.m.r. spectrum of the dihydropyridazinone (6).[3]

The tetrahydropyridazinone (7) could be prepared more conveniently by reduction of the dihydropyridazinone (6) with sodium cyanotrihydridoborate.[4] Elemental analysis as well as mass, i.r., and ^{1}H n.m.r. spectra confirmed the structure (7).

When the tetrahydropyridazinone (7) was kept at room temperature with 1 equiv. of dimethyl acetylenedicarboxylate, pale yellow crystals of the anilinoazepinone (10) identified on the basis of analysis and spectral data, were formed. Comparison of spectral data for the azepinone (10) and the diazepinone (5) [2] was instructive. The ^{13}C n.m.r. spectrum of the azepinone (10) established that ring expansion had taken place by insertion of the ester between a nitrogen atom and the carbonyl group of the pyridazinone (7). The carbonyl absorption at δ 198.9 indicated that it was now an αβ-unsaturated carbonyl function, and the signal at δ 104.4 can be assigned to the olefinic carbon atom β to a nitrogen.[2,5] The chemical shifts for the aromatic carbon atoms (δ 145.5 for C–N, 115.1 for the *ortho*-C, 129.5 for *meta*-C, and 122.6 for *para*-C) much more closely resemble those reported for similar carbon atoms in aniline and phenylhydrazine than those for acetanilide and *N*-nitrosomethylaniline.[6] The chemical shifts for



(1) R = Ph
(2) R = PhCH$_2$
(3) R = Ph
(4) R = PhCH$_2$
(5) R = Ph, E = CO$_2$Me

SCHEME 1

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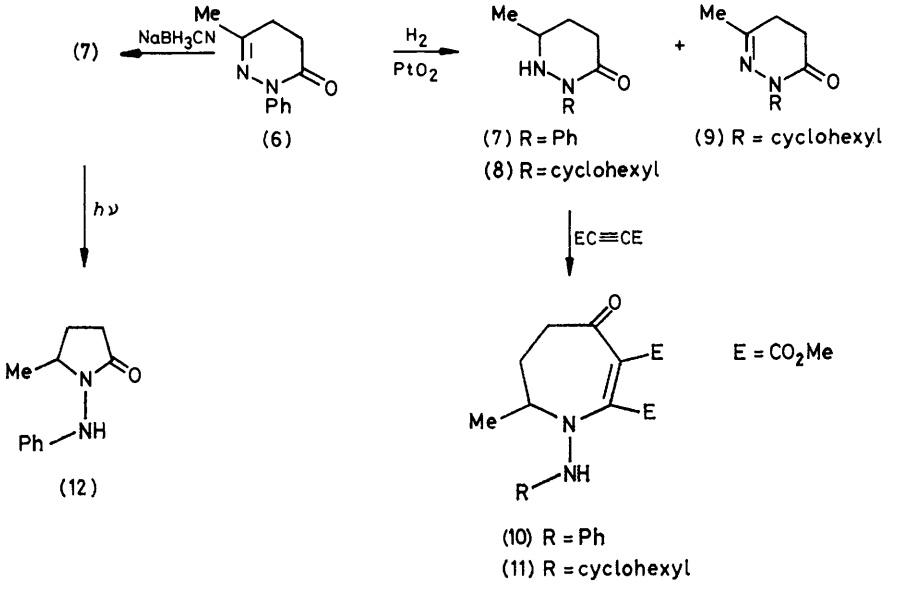
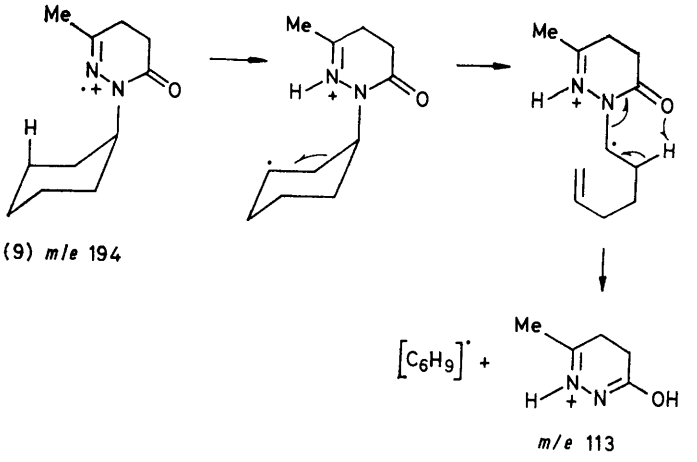
[3] J. L. Aubagnac, J. Elguero, R. Jacquier, and R. Robert, *Bull. Soc. chim. France*, 1972, 2859.
[4] R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Amer. Chem. Soc.*, 1971, **93**, 2897.
[5] J. B. Stothers, 'C-13 Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1972.
[6] L. F. Johnson and W. C. Jankowski, 'C-13 NMR Spectra,' Wiley, New York, 1972.

the aromatic carbon atoms in the diazepinone (5) reflect the conjugation with electron-withdrawing substituents, and its olefinic carbon atom β to the nitrogen is more deshielded (δ 114.0).[2] Together these facts point to a structure in which the nitrogen bearing the phenyl group is outside the ring in the azepinone (10) in contrast to a structure with both nitrogen atoms incorporated into an eight-membered ring. The ^{1}H n.m.r. spectrum of the azepinone (10) shows a multiplet for the aryl protons which comes further upfield, δ 6.8—7.3, than the singlet, δ 7.3, which appears for the aryl protons of the diazepinone (5). The proton on nitrogen which gives rise to a doublet at δ 4.8 in the spectrum of the diazepinone (5) is not visible in that of the azepinone (10), and may be buried under the multiplet for the aryl protons, as observed for a similar proton in *N*-anilinoazetidinones.[7] Chemical shifts close to these have been reported for similar protons in phenylhydrazides.[8] The azepinone (10) shows complex carbonyl i.r. absorption in the region 1 745—1 675 cm^{-1}. Its mass spectrum has $C_6H_5NH^+$ for the base peak (*m/e* 92), which decomposes *via* a metastable ion (*m/e* 46) to $C_5H_5^+$ (*m/e* 65).



SCHEME 2

Dissolution of the diazepinone (5) in trifluoroacetic acid or in benzene containing toluene-*p*-sulphonic acid almost instantly gives ring contraction products (phenylpyrazoles) resulting from transannular reactions between the nitrogen unsubstituted with the phenyl group and the carbonyl group.[2] However the anilinoazepinone (10), after 24 h in trifluoroacetic acid, was recovered unchanged. Transannular interactions between nitrogen and carbonyl groups in eight-membered ring systems have been detected spectroscopically.[9] If a diazocinone



SCHEME 3

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[8] H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977; P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 3502.
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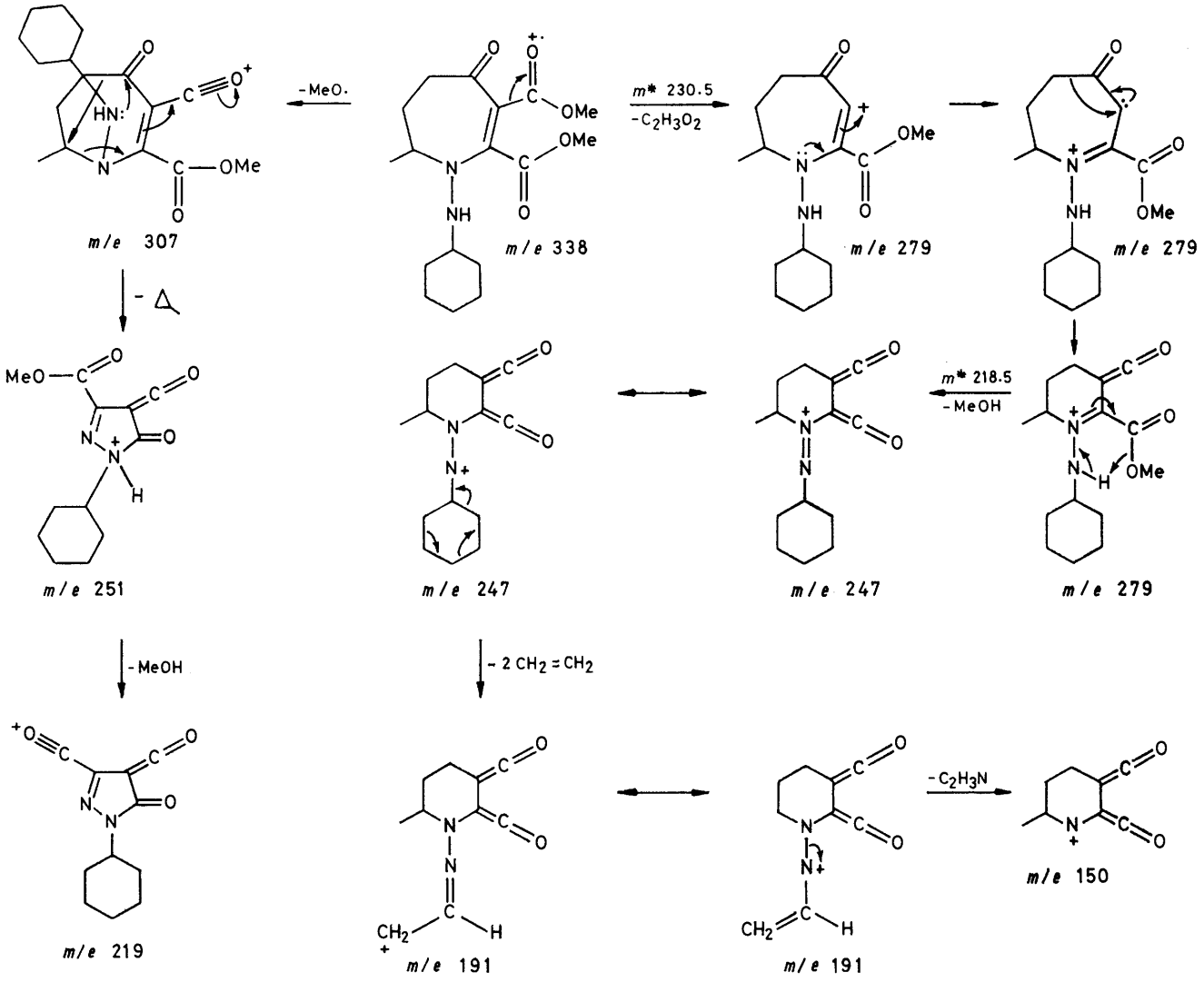
system had been present, we would have expected to see the kind of ring contraction observed with the diazepinones.

The ring expansion observed with pyrazolidinones did not take place when 2-benzyl-5-methylpyrazolidin-3-one (2) was used (Scheme 1). Here the sole product was the oxopyrazolidinylmaleic ester (4), identified on the basis of analysis and its ^{1}H n.m.r. spectrum [δ 5.2 (vinylic H)].[2,10] The signal of the benzylic protons (almost a singlet in the spectrum of the parent pyrazolidinone) appears as an AB multiplet centred at δ 5.1, a feature typical of benzylpyrazolidinones with a chiral centre on an adjacent carbon atom, or with adjacent *N*-substituents which slow the nitrogen inversion.[11] The methyl signal appears at unusually high field (δ 0.45). Upfield shifts, though none this extreme, of methyl groups in benzylpyrazolidinones have been observed and have been attributed to conformations of the benzyl group within the molecule in which the phenyl ring shields the methyl group across the heterocycle.[11]

In contrast to the pyrazolidinone case where an alkyl substituent on N-2 completely inhibited ring expansion, the cyclohexyltetrahydropyridazinone (8) reacted with dimethyl acetylenedicarboxylate to give the cyclohexylaminoazepinone (11). The ^{13}C n.m.r. spectrum compound (11) shows insertion of the ester between nitrogen and carbonyl, with signals at δ 198.3 for an αβ-unsaturated carbonyl group and at δ 103.3 for the olefinic carbon atom β to nitrogen. The parent pyridazinone (8) shows equivalence of two pairs of cyclohexyl carbon atoms, but in the azepinone (11) restricted rotation of the cyclohexyl group around the carbon–nitrogen bond becomes evident, with different chemical shifts for all the carbon atoms in the molecule. The ^{1}H n.m.r. spectrum of the azepinone (11) has a band at δ 4.4



SCHEME 4

[10] J. E. Dolfini, *J. Org. Chem.*, 1965, **30**, 1298; K. Herbig, R. Huisgen, and H. Huber, *Chem. Ber.*, 1966, **99**, 2546.

[11] J. Elguero, C. Marzin, and D. Tizane, *Org. Magnetic Resonance*, 1969, **1**, 249.

(singlet) which is removed in D_2O. The carbonyl region of the i.r. spectrum is complex, with major absorptions at 1 740 and 1 650 cm^{-1}. The azepinone (11) can be recovered unchanged from solution in trifluoroacetic acid, though there are downfield shifts of the signals due to methine protons and the protons which appear to be adjacent to the carbonyl group in its ^1H n.m.r. spectrum in that solvent.

The mass spectrum of the azepinone (11) seems to be the most informative in determining whether ring expansion has taken place to a seven- or an eight-membered ring. Scheme 4 shows an interpretation of the origins of some of the major peaks. Especially significant is the metastable ion, *m/e* 218.5, which points to the loss of methanol by migration of a hydrogen atom from the cyclohexylamino-group. This migration is hard to rationalize in the case of an eight-membered ring structure. Ions *m/e* 251 and 219 correspond to ions *m/e* 245 and 213 in the mass spectrum of the anilino-azepinone (10), and support the assignment of a similar type of structure to the cyclohexyl compound. Finally, there is an important peak at *m/e* 98 which would correspond to the cleavage of the nitrogen–nitrogen bond in an ion such as that at *m/e* 279.

For the reaction mechanism we had postulated a bicyclic intermediate, considered to result from attack by a carbanion (produced by Michael addition of the secondary amine group in the pyrazolidinones to the dimethyl acetylenedicarboxylate) on the pyrazolidinone carbonyl, and its subsequent opening and ring expansion.[2] In the case of the tetrahydropyridazinones, no products resulting from the simple Michael addition of the amine to the ester, such as the maleate esters (3) and (4), are seen. The reaction goes cleanly to the product that results from ring opening of the bicyclic intermediate without further ring expansion to a diazocine.

We were interested in comparing the photochemistry of tetrahydropyridazinones with that of pyrazolidinones, which undergo ring contraction to *N*-aminoazetidinones,[7,12] in contrast with pyrazolinones, which undergo transposition of their ring atoms upon irradiation.[7,13] Pyridazinones undergo a variety of thermal ring contraction reactions, mostly to pyrazole and pyrrole systems, depending on the substituents present and the reagents used.[14] Tsuchiya and his co-workers have reported the conversion of pyridazin-3(2*H*)-ones into 1-amino-Δ^3-pyrrolin-2-ones, and 6-methyl-4,5-dihydropyridazin-3(2*H*)-one is reported to give only methyl levulinate, in low yield, upon irradiation in methanol.[15] The tetrahydropyridazinone (7) behaves in a manner analogous to the pyrazolidinones, giving *N*-anilino-5-methylpyrrolidin-2-one (12) (Scheme 2) upon irradiation in methanol. The structure of the compound is supported by its mass spectrum with the molecular ion at *m/e* 190, and the base peak at *m/e* 92 ($C_6H_5NH^+$). The ^{13}C n.m.r. spectrum once again has chemical shifts for the aromatic carbon atoms that are compatible with an exocyclic anilino-group. The change in the carbonyl i.r. frequency from 1 675 cm^{-1} in the tetrahydropyridazinone (7) to 1 700 cm^{-1} in the anilinopyrrolidinone (12) also points to a ring contraction reaction. The ^1H n.m.r. spectrum shows a phenomenon also observed for *N*-anilinoazetidinones:[7] the chemical shift of the proton on nitrogen is solvent-dependent, appearing at δ 6.3 in deuteriochloroform and underneath the aryl multiplet in carbon tetrachloride.

Compound (12) was obtained as a viscous oil, and in spite of repeated chromatography and Kugelrohr distillations, could not be made to crystallize. Analyses consistently gave values that were correct for nitrogen and hydrogen but below the acceptable value for carbon; the samples had correct molecular ions in mass spectra. We are satisfied from the spectral data that the structure is as assigned.

EXPERIMENTAL

M.p.s were determined for samples in capillaries with a Thomas-Hoover apparatus. I.r. spectra were recorded with a Perkin-Elmer 237B spectrophotometer. ^1H N.m.r. spectra were recorded with a Varian T-60 spectrometer; ^{13}C n.m.r. spectra were obtained with a PFT 100 25.2 MHz Fourier transform n.m.r. spectrometer (tetramethylsilane internal standard was used for both). Mass spectra were obtained with an A.E.I. MS902 spectrometer.

For chromatographic separations, alumina refers to Woelm neutral alumina, grade II, unless otherwise specified. Analytical t.l.c. was carried out on Eastman Chromagram sheets of silica gel and alumina, with or without fluorescent indicator. Solvents were all reagent grade. All evaporations were carried out with a rotary evaporator under vacuum.

4,5-Dihydro-6-methyl-2-phenylpyridazin-3(2H)-one (6).—The dihydropyridazinone (6) was prepared by heating phenylhydrazine (4.43 g, 41 mmol) and levulinic acid (4.76 g, 40 mmol) to 170 °C.[3] Recrystallization of the solid formed gave cream-coloured crystals (3.33 g, 44%), m.p. 106—107° (from ethanol) (lit.,[3] 106—107°); δ ($CDCl_3$) 2.1 (3 H, s), 2.5 (4 H, s), and 7.4 (5 H, m):[3] δ_H (benzene) 1.8 (3 H, s) and 2.4 (4 H, m); $\nu_{max.}$ ($CHCl_3$) 3 000, 1 670, 1 655sh, 1 600, 1 500, 1 425, 1 375, 1 330, 1 045, and 940 cm^{-1}.

6-Methyl-2-phenyltetrahydropyridazin-3-one (7).—The dihydropyridazinone (6) (3.6 g, 20 mmol) in methanol (160 ml) was reduced with sodium cyanotrihydridoborate (Aldrich; 2.52 g, 40 mmol) at pH 3—4 (Bromcresol Green; 2N-hydrochloric acid in methanol added as necessary) according to the directions of Borch *et al.*[4] The reduction was complete in 2 h. The mixture was made basic (pH 9) with 2N-potassium hydroxide in methanol. Evaporation gave a mixture of a white solid and a yellow oil. This was repeatedly extracted with methylene chloride. The combined organic extracts were dried ($MgSO_4$) and evaporated to give the *tetrahydropyridazinone* (7) (1.51 g, 40%), m.p.

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[14] H. C. van der Plas, ' Ring Transformations of Heterocycles,' vol. 2, Academic Press, New York, 1973, pp. 146—152.
[15] T. Tsuchiya, M. Hasebe, H. Arai, and H. Igeta, *Chem. and Pharm. Bull. (Japan)*, 1974, **22**, 2276.

68—69° (from hexane) (Found: C, 69.5; H, 7.4; N, 14.7. $C_{11}H_{14}N_2O$ requires C, 69.4; H, 7.4; N, 14.7%); *m/e* 190 (M^+, base), 175, 162, 147, 135, 119, 104, 92, 77, 70, 51, and 41; *m** 161.2 (190 → 175), 133 (162 → 147), and 118.5 (147 → 132); $\nu_{max.}$ ($CHCl_3$) 3 000, 2 940, 2 860, 1 675, 1 600, 1 500, and 1 380 cm^{-1}; δ_H ($CDCl_3$) 1.1 (3 H, d, *J* 6 Hz), 2.3 (4 H, m), 3.2 (1 H, m), 4.3 (1 H, d, *J* 7 Hz), and 7.4 (5 H, m).

Hydrogenation of the Dihydropyridazinone (6).—The dihydropyridazinone (6) (3 g) was hydrogenated overnight in glacial acetic acid (80 ml) over platinum oxide (500 mg) at 3 atm in a Parr apparatus.[16] The solvent was removed by vacuum distillation and the residue chromatographed on alumina (150 g). After the column had been developed with benzene (300 ml), further elution gave the tetrahydropyridazinone (7) (1.28 g) [absolute ether (530 ml)], and 2-*cyclohexyl*-6-*methyltetrahydropyridazin*-3-*one* (8) (462 mg) [eluted with anaesthesia ether (300 ml)], m.p. 58.5—59° (from hexane) (Found: C, 67.3; H, 10.2; N, 14.3. $C_{11}H_{20}N_2O$ requires C, 67.3; H, 10.3; N, 14.3%); *m/e* 196 (M^+), 181, 153, 141, 125, 114 (base), 99, 85, 69, 67, 59, 55, and 41; *m** 86 (114 → 99) and 66.3 (196 → 114); δ_H ($CDCl_3$) 1.1 (3 H, d, *J* 6 Hz), 1.6 (12 H, m), 2.3 (2 H, t), 3.2 (2 H, m), and 4.2 (1 H, m); $\nu_{max.}$ ($CHCl_3$) 3 000, 2 925, 2 850, 1 640, 1 625, 1 525, 1 450, 1 410, 1 040, and 925 cm^{-1}; δ_C ($CDCl_3$) 19.66, 25.42, 29.18, 29.49, 29.61, 30.94, 50.84, 53.09, and 171.0.

In another hydrogenation where additional catalyst was used when t.l.c. (Al_2O_3; benzene, developed twice) showed the presence of the dihydropyridazinone (6) after 2 h of reaction and the reaction was continued overnight, an n.m.r. spectrum gave a very weak aromatic proton signal. Chromatography of the residue (5.3 g) left after removal of the solvent, on alumina (100 g), after development with benzene (200 ml), gave a mixture (956 mg) [eluted with absolute ether (200 ml)] of the tetrahydro- (8) and the dihydro-cyclohexylpyridazinone (9). Further elution, with anaesthesia ether (220 ml), yielded the tetrahydrocyclohexylpyridazinone (8) (1.42 g).

Rechromatography of the mixture (523 mg) on alumina (30 g) separated the dihydrocyclohexylpyridazinone (9) (198 mg) [eluted with ether–benzene (1 : 1; 40 ml) after development with benzene (60 ml)] and the tetrahydrocyclohexylpyridazinone (8) (300 mg) [eluted with anaesthesia ether (60 ml)]. 2-*Cyclohexyl*-4,5-*dihydro*-6-*methylpyridazin*-3(2H)-*one* (9) was isolated as white crystals, m.p. 54.5—55° (from pentane) (Found: C, 68.2; H, 9.2; N, 14.5. $C_{11}H_{18}N_2O$ requires C, 68.0; H, 9.3; N, 14.4%); *m/e* 194 (M^+), 179, 177, 151, 125, 113 (base), 112, 110, 98, 84, 83, 82, 69, 68, 67, 55, and 41; δ_H (CCl_4) 1.5 (10 H, m), 2.0 (3 H, s), 2.3 (4 H, s), and 4.3 (1 H, m); $\nu_{max.}$ ($CHCl_3$) 3 010, 2 925, 2 850, 1 640, 1 525, 1 440, 1 415, 1 350, 1 050, and 940 cm^{-1}.

Reactions of Tetrahydropyridazinones with Dimethyl Acetylenedicarboxylate.—(a) *Dimethyl* 1-*anilino*-4,5,6,7-*tetrahydro*-7-*methyl*-4-*oxo*-1H-*azepine*-2,3-*dicarboxylate* (10). The tetrahydropyridazinone (7) (198 mg, 1.04 mmol) and dimethyl acetylenedicarboxylate (185 mg, 1.30 mmol) were kept in carbon tetrachloride (3 ml) for 1 day, after which t.l.c. (silica gel; chloroform) indicated that the reaction was complete. Evaporation gave the *azepinone* (10) (157 mg, 46%), m.p. 177—178° (from methanol) (Found: C, 61.4; H, 6.0; N, 8.4. $C_{17}H_{20}N_2O_5$ requires C, 61.4; H, 6.1; N, 8.4%); *m/e* 332 (M^+), 301, 245, 244, 241, 240, 213, 93, 92 (base), 91, 77, 65, and 55; *m** 272.9 (332 → 301), 191.4 (301 → 240), and 46 (92 → 65); $\nu_{max.}$ ($CHCl_3$) 3 300, 1 745, 1 725, 1 675, 1 603, 1 550, 1 500, and 1 440 cm^{-1}; δ_H ($CDCl_3$) 1.3 (3 H, d, *J* 6 Hz), 2.0—3.2 (4 H, m), 3.7 (7 H, s on m), and 6.8—7.3 (5—6 H, m); δ_H ($CF_3{\cdot}CO_2H$) 1.4 (3 H, d, *J* 6 Hz), 2.1—3.2 (4 H, m), 3.8 (6 H, s), 4.3 (1 H, m), and 6.8—7.2 (5 H, m); sample recovered with minor changes by dilution with water and extraction into chloroform after 24 h in the acid; δ_C ($CDCl_3$) 16.26 (q), 41.07 (t), 52.06 (m), 52.78 (m), 61.40 (d), 104.4 (s), 115.1 (d), 122.6 (d), 129.5 (d), 145.5 (s), 164.5 (s), 166.5 (s), and 198.9 (s).

(b) *Dimethyl* 1-*cyclohexylamino*-4,5,6,7-*tetrahydro*-7-*methyl*-4-*oxo*-1H-*azepine*-2,3-*dicarboxylate* (11). The tetrahydrocyclohexylpyridazinone (8) (300 mg, 1.53 mmol) and dimethyl acetylenedicarboxylate (260 mg, 1.83 mmol) were kept in carbon tetrachloride (5 ml) at room temperature for 5 days. Removal of the solvent left *crystals* (487 mg, 94%), m.p. 126—127° (from cyclohexane–benzene) (Found: C, 60.3; H, 7.8; N, 8.3. $C_{17}H_{26}N_2O_5$ requires C, 60.3; H, 7.7; N, 8.3%); *m/e* 338 (M^+, base), 307, 291, 279, 263, 251, 247, 235, 224, 219, 191, 181, 169, 168, 165, 150, 126, 111, 98, 83, 69, 59, and 55; *m** 230.5 (338 → 279) and 218.5 (279 → 247); δ_H (CCl_4) 1.5 (3 H, d, *J* 6 Hz), 1.9—3.5 (16 H, m), 3.7 (3 H, s), 3.9 (3 H, s), and 4.4 (1 H, s, exchanged with D_2O); δ_H (CF_3COOH) 1.8 (3 H, d, *J* 6 Hz), 1.0—2.4 (10 H, m), 2.8—3.4 (5 H, m), 4.1 (3 H, s), 4.2 (3 H, s), and 4.4—5.0 (2 H, m); sample recovered essentially unchanged after dilution with water and extraction with chloroform after 48 h in acid; $\nu_{max.}$ ($CHCl_3$) 3 450, 1 740, 1 650, and 1 530 cm^{-1}; δ_C ($CDCl_3$) 16.26, 24.21, 24.51, 25.66, 31.06, 31.49, 40.89, 41.86, 51.69, 52.42, 59.34, 62.91, 103.3, 163.1, 164.5, 166.3, and 198.3.

Photolysis of 6-*Methyl*-2-*phenyltetrahydropyridazin*-3-*one* (7).—The tetrahydropyridazinone (7) (500 mg) was irradiated in anhydrous methanol (165 ml) in two Vycor tubes at 254 nm in a Rayonet apparatus for *ca.* 10 h. Removal of the solvent and chromatography of the residue on alumina (30 g) gave 1-*anilino*-5-*methylpyrrolidin*-2-*one* (12) (300 mg) [eluted with anaesthesia ether (150 ml) after the column had been developed with benzene (200 ml) and benzene–ether (95 : 5; 250 ml)], which was purified further by Kugelrohr distillation, trituration of distilled material with hexane, and Kugelrohr distillation of the hexane-soluble portion at 0.5 mmHg to give a viscous oil which could not be induced to crystallize (Found: C, 68.6, 68.6, 68.6; H, 7.2, 7.3, 7.3; N, 14.5, 14.4, 14.5. $C_{11}H_{14}N_2O$ requires C, 69.4; H, 7.4; N, 14.7%); *m/e* 190 (M^+, base), 175, 162, 148, 147, 134, 120, 119, 118, 108, 106, 105, 92, 77, 65, 56, 51, 41, 39, 28, 27, and 18; *m** 161.2 (190 → 175), 133.3 (162 → 147), 123.5 (175 → 147), 115.3 (190 → 148), 63.2 (134 → 92), and 46 (92 → 65); $\nu_{max.}$ ($CHCl_3$) 3 300, 1 700, 1 603, and 1 500 cm^{-1}; δ_H ($CDCl_3$) 1.2 (3 H, d, *J* 6 Hz), 2.0 (2 H, m), 2.4 (2 H, m), 3.8 (1 H, m), 6.3 (1 H, s), and 6.8—7.4 (5 H, m); δ_H (CCl_4) 6.4—7.4 (6 H, m); δ_C ($CDCl_3$) 18.87, 24.82, 27.99, 54.52, 113.3, 120.7, 128.9, 146.4, and 174.1.

Reaction of 2-*Benzyl*-5-*methylpyrazolidin*-3-*one* (2) *with Dimethyl Acetylenedicarboxylate.*—The pyrazolidinone (2)[11] (967 mg, 5.12 mmol) and dimethyl acetylenedicarboxylate (800 mg, 5.63 mmol) were refluxed in acetonitrile (60 ml; dried by distillation from calcium hydride) for 3 h; the mixture was set aside overnight, then heated again for 1 h with an additional two drops of ester. T.l.c. (alumina;

[16] T. R. Lynch, M. N. Maclachlan, and Y. K. Siu, *Canad. J. Chem.*, 1971, **49**, 1598.

chloroform) showed one product, which was isolated by evaporation and finally evacuation to 1 mmHg for 2.5 h. *Dimethyl (2-benzyl-5-methyl-3-oxopyrazolidinyl)maleate* was isolated as white crystals, m.p. 95.5—96.5° (from n-heptane) (Found: C, 61.2; H, 6.2; N, 8.5. $C_{17}H_{20}N_2O_5$ requires C, 61.4; H, 6.1; N, 8.4%); *m/e* 332 (M^+), 301, 273, 241, 209, 200, 199, 186, 181, 174, 140, 132, 106, 99, 92, 91 (base), 77, 69, 65, and 53; *m** 224.5 (332 ⟶ 273), 181.3 (241 ⟶ 209), and 156.8 (209 ⟶ 181); δ_H ($CDCl_3$) 0.45 (3 H, d, *J* 6 Hz), 1.9 (1 H, m), 2.9 (1 H, m), 3.7 (3 H, s), 3.9 (3 H, s), 4.0 (1 H, m), 5.1 (2 H, m), 5.2 (1 H, s), and 7.4 (5 H, s); $\nu_{max.}$ ($CHCl_3$) 1 750, 1 700, 1 603, 1 445, 1 370, and 1 160 cm^{-1}.

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