Azepinones. Part 4.[1,2] Electrocyclic and Cycloaddition Reactions of Simple 1*H*-Azepin-3(2*H*)-ones

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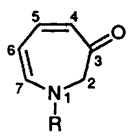
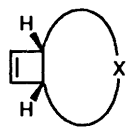
Photolysis of the azepinone (**2**) gives the bicyclic photoproduct (**5**) in 64% yield; this compound reverts cleanly to the starting material (**2**) on thermolysis in toluene. Cycloaddition reactions of the azepinones (**1**) or (**2**) with maleic anhydride generate the *endo* adducts (**7**) or (**8**), respectively, whereas treatment of (**1**) with acetylenic dienophiles gives rise to benzenoid compounds after cleavage of the three-atom bridge.

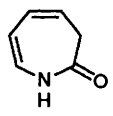
We continue our studies of the chemistry of 1*H*-azepin-3(2*H*)-ones (**1**) and (**2**)[1-3] by describing the activity of the conjugated diene unit [C(4)–C(7)] in pericyclic processes, including photochemical ring contraction and cycloaddition reactions. These have considerable precedent in the reactivity of heterocyclic dienes. Thus, for example, fused cyclobutenes (**3**) have been obtained from photochemical disrotatory electrocyclisation of the diene unit in pyridones,[4] pyrones,[4] azepines,[5] oxepines,[6] and benzothiepins,[7] as well as from the 1*H*-azepin-2(3*H*)-one system (**4**)[8-10] which is isomeric with our compounds.



(**1**) R = Me
(**2**) R = Ph



(**3**) X = heteroatom



(**4**)

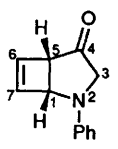
Similarly, treatment with selected dienophiles gives Diels–Alder cycloadducts from pyridones,[11] and the azepinones (**4**).[12] In the case of pyrones, the initial cycloaddition is often followed by collapse of the bridge leading to the formation of benzenoid compounds.[13]

Results and Discussion

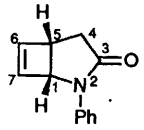
Photolysis.—Irradiation of a solution of the 1-phenylazepinone (**2**) in [$^2H_6$]acetone with a 125 W Hg lamp gave a single major product which was isolated in 64% yield by dry flash chromatography as a thermally unstable solid. The mass spectrum shows that this product is an isomer of the starting material and its structure follows from an analysis of its NMR spectra. Thus the signals due to the diene unit in (**2**) have been replaced by a pair of olefinic doublets [δ_H 6.60 (1 H) and 6.33 (1 H); δ_C 141.06 and 137.13] and a pair of aliphatic doublets [δ_H 4.99 (1 H) and 3.80 (1 H); δ_C 60.23 and 54.55] while the chemical shift of the carbonyl carbon atom (δ_C 207.92) is typical of that in saturated 5-membered rings.[14] These data are consistent with the expected bicycloheptenone structure (**5**). Full assignment of the ^{1}H NMR spectrum was made by a series of NOE experiments which serve to distinguish the related protons at positions 1 and 5 and at positions 6 and 7 (Fig. 1). Irradiation of the *ortho* aromatic signals gave significant enhancement of the *meta*-proton signals, the methylene signals, and the peak at δ_H 4.99 (15%) which is accordingly identified as being due to the 1-position. Irradiation of the *other* aliphatic signal (δ_H 3.80, 5-position) causes enhancement at the 1-position (as expected for *cis*-fused rings) and also of the olefinic signal at δ_H 6.33, which is therefore identified as being due to the 6-position. The non-equivalent methylene protons (3-H) could not be distinguished by these experiments, but otherwise the complete assignments are shown in Fig. 1.

The coupling pattern given in Fig. 1(*c*) was established by a comprehensive series of decoupling experiments. Notable features include long-range coupling (^4J *ca.* 1 Hz) between each geminally non-equivalent methylene proton and an individual ring junction proton, and the failure of the olefinic proton 7-H to couple to *either* of the ring junction protons (1-H or 5-H) though its olefinic partner (6-H) couples to both ($^3J_{5,6}$ and $^4J_{1,6}$ 1.2 Hz).

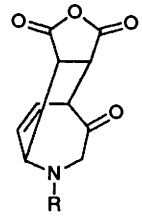
The bicyclic compound (**5**) was reasonably stable at room temperature and below, but attempted recrystallisation or distillation led only to recovery of the azepinone (**2**). Although concerted disrotatory thermal ring opening is formally disallowed, such behaviour is well known for the bicyclic photoproducts (**3**), some of which can only be detected at low temperatures.[15] The thermal ring opening of compound (**5**) in [$^2H_8$]toluene was followed by ^{1}H NMR spectroscopy, in the probe of the spectrometer and shows good first order kinetics at temperatures of 78 °C and 84.5 °C (k 8.9 ± 0.23 and 14.0 ± 0.25 × 10^{-3} min^{-1}, respectively) (Fig. 2) from which the activation energy for the process may be estimated as *ca.* 72.4 kJ mol^{-1}. This ring opening is much more facile than for the isomeric system (**6**) which requires flash vacuum pyrolysis at



(**5**)



(**6**)



(**7**) R = Me
(**8**) R = Ph

430 °C to cause reversion to the azepinone.[8] Push–pull substitution of the incipient diene—found in the hepten-4-one (**5**) but not in the hepten-3-one (**6**)—is known to favour 'forbidden' ring opening processes.[16] Alternatively, lone-pair assisted cleavage of the C(1)–C(5) bond (Scheme 1) is possible only with the hepten-4-one isomer.

Cycloadditions.—The diene unit of 1*H*-azepin-3(2*H*)-ones is also reactive towards dienophiles. For example, the 1-phenyl compound (**2**) was found to react with maleic anhydride over a

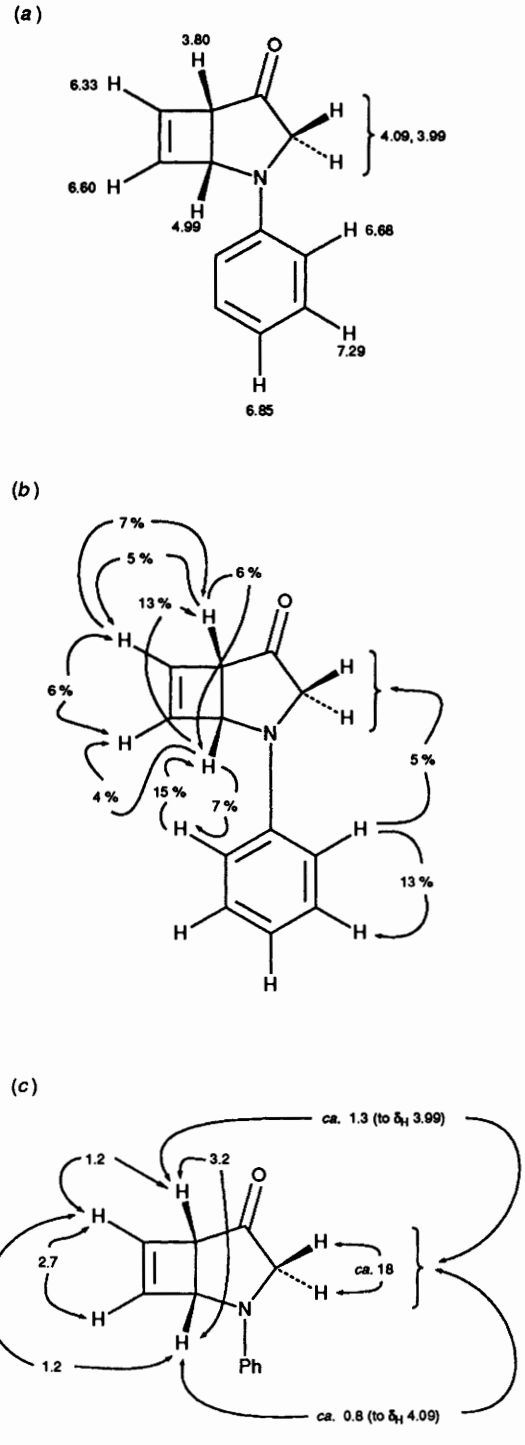


Fig. 1. ^{1}H NMR parameters of (**5**): (*a*), chemical shifts; (*b*), NOE (irradiation at 'arrow tail' positions); (*c*), coupling constants (J_{HH}/Hz).

period of 48 h, at room temperature, in benzene to give the cycloadduct (**8**) as a solid, which could be recrystallised from methanol (64%). These mild conditions contrast dramatically with those employed in the reaction of 1-methyl-1*H*-pyridin-2-one (110 °C, 72 h)[11] and the complete absence of reaction with the isomeric azepin-2-one.[12] Reaction of the 1-methylazepinone occurs even more rapidly: the product, (**7**) (81%), was produced in less than 2 h at room temperature, but it was unstable to heat and in solution, decomposing to an unidentified, very insoluble material. The variation in reaction rate observed when the nitrogen atom substitution is changed indicates that the diene

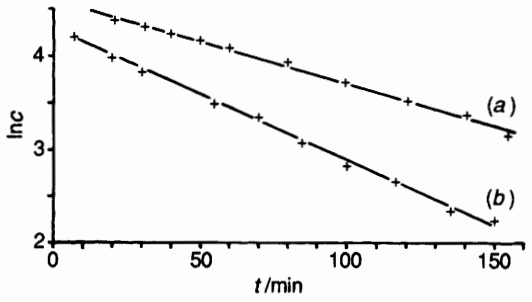
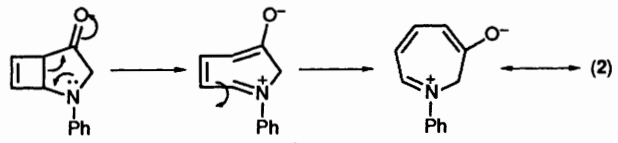


Fig. 2. First order plots for the thermal ring opening of (**5**): (*a*), at 78 °C; and (*b*), at 84.5 °C.



Scheme 1.

unit is participating in the reaction as a typical, electron-rich system reacting with the electron-poor dienophile. The *N*-methyl group has better electron-donating abilities than the *N*-phenyl, whereas in the analogous pyridin-2-one and azepin-2-one systems the nitrogen atom has amide character which drastically reduces this donating effect.

The structures of the cycloadducts (**7**) and (**8**) follow in particular from their ^{1}H NMR spectra, analysed in detail for the *N*-phenyl derivative (**8**). At 360 MHz, this spectrum shows two triplets (δ_H 7.31 and 6.89) and a doublet (δ_H 7.02) corresponding to the *meta*, *para*, and *ortho* protons, respectively, of the aromatic ring. The two alkene protons give rise to a complicated overlapping multiplet at δ_H 6.63, whereas the six aliphatic protons appear as a pair of doublets (δ_H 4.32 and 4.02), a pair of doublets of doublets (δ_H 4.09 and 3.83), and a pair of doublets of apparent triplets (δ_H 5.12 and 3.72). The unambiguous assignment of these resonances follows from a series of NOE experiments. In particular, irradiation of the *ortho* protons of the phenyl group causes enhancement of the doublet of triplets at δ_H 5.12 (12.5%) (which is therefore due to the bridgehead proton adjacent to the nitrogen atom), enhancement of both doublets [δ_H 4.32 (1.5%) and 4.02 (5.2%)] (which are therefore due to the methylene protons and hence these must lie *s*-*Z* to the phenyl group), and finally enhancement of the doublet of doublets at δ_H 4.09 (3.5%) (which must therefore be due to a ring junction proton). This last result is of special significance since it shows that the geometry of ring fusion must be *endo*, and in addition that both the phenyl and the methylene groups lie in the neighbourhood of these ring junction protons rather than over the olefinics. The results were confirmed by irradiation of the methylene protons: only that at δ_H 4.02 produced an effect at the ring junction [δ_H 3.83 (2%)], whereas that at δ_H 4.32 had negligible effect on either the alkene or the ring-junction protons. The configuration and conformation of the molecule are therefore as shown in Fig. 3, where the assignment of the ^{1}H NMR spectrum is displayed, and the important NOE results are summarised. The coupling pattern [Fig. 3(*c*)] was mostly deduced by inspection, though a double resonance experiment confirmed that the coupling between the bridgehead and ring-junction protons is small (*ca.* 2.0 Hz).

Flash vacuum pyrolysis of the 1-phenyl adduct (**8**) at 600 °C (10^{-3} mmHg) gave the 1-phenylazepinone and maleic anhydride with no evidence (by ^{1}H NMR spectroscopy or GC analysis) of other fragmentation products. A similar retro-Diels–Alder reaction is displayed in the mass spectra of the cycloadducts (**7**) and (**8**).

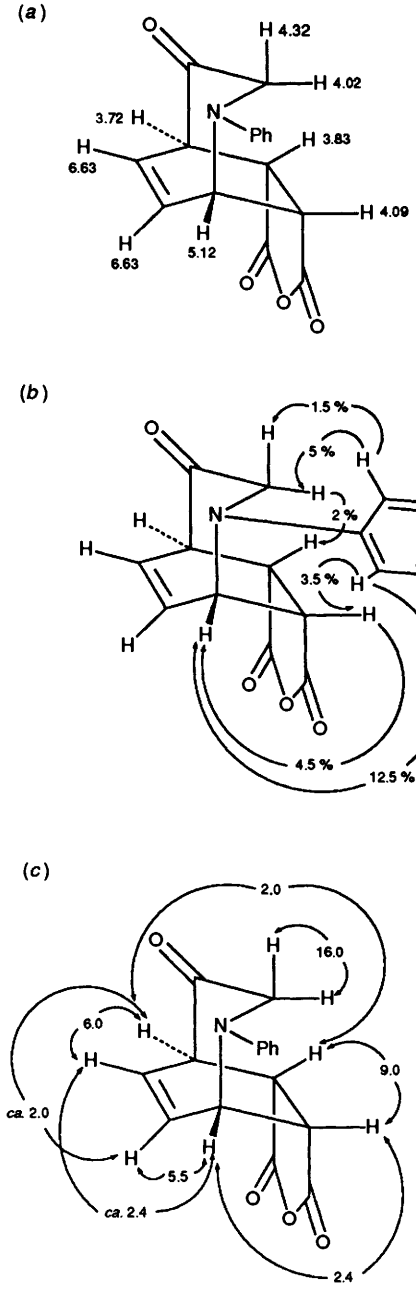
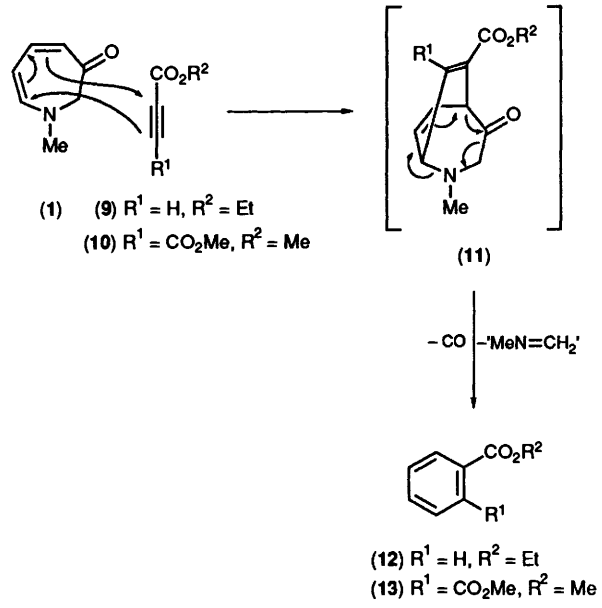


Fig. 3. ^{1}H NMR parameters of (**8**): (*a*), chemical shifts; (*b*), NOE (irradiation at 'arrow tail' positions); and (*c*), coupling constants (J_{HH}/Hz).

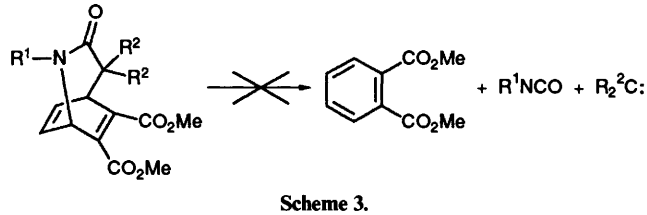
Reactions of the azepinones (**1**) and (**2**) with other olefinic dienophiles were generally less successful than those with maleic anhydride (see Experimental section). However, treatment of the 1-phenyl compound (**2**) with tetracyanoethylene in methanol gave an instantaneous precipitate of a yellow solid. The solid was extremely insoluble, and when attempts were made to recrystallise it, bright red solutions resulted from which no product could be obtained. A ^{1}H NMR spectrum of the solid, obtained immediately on dissolution in [$^2H_6$]DMSO, showed only signals corresponding to the starting azepinone. An IR spectrum of the solid showed a carbonyl absorption at 1615 cm^{-1} which is consistent with an extended amide such as the starting material, in contrast to the typical saturated ketone value (ν_{max} > 1700 cm^{-1}) of the maleic anhydride adducts. Though these data are consistent with the formation of a charge transfer complex between the diene and dienophile, the mass spectrum of the material shows a weak (< 0.01%) peak corresponding to the molecular ion of the expected cycloadduct (Found: M^+ 313.0970. $C_{18}H_{11}N_5O$ requires 313.0964). The exact constitution of this material remains unknown.

The *N*-methylazepinone (**1**) was sufficiently activated to react with the acetylenic dienophiles, ethyl propiolate (**9**) and dimethyl acetylenedicarboxylate (DMAD) (**10**), though in both cases the major product was a benzene derivative and not the expected cycloadduct. Thus treatment of a solution of azepinone (**1**) in acetonitrile with dienophiles (**9**) (16 h reflux) or (**10**) (6 d 20 °C) gave respectively, ethyl benzoate (**12**) (80%) and dimethyl phthalate (**13**) (73%) (Scheme 2). The



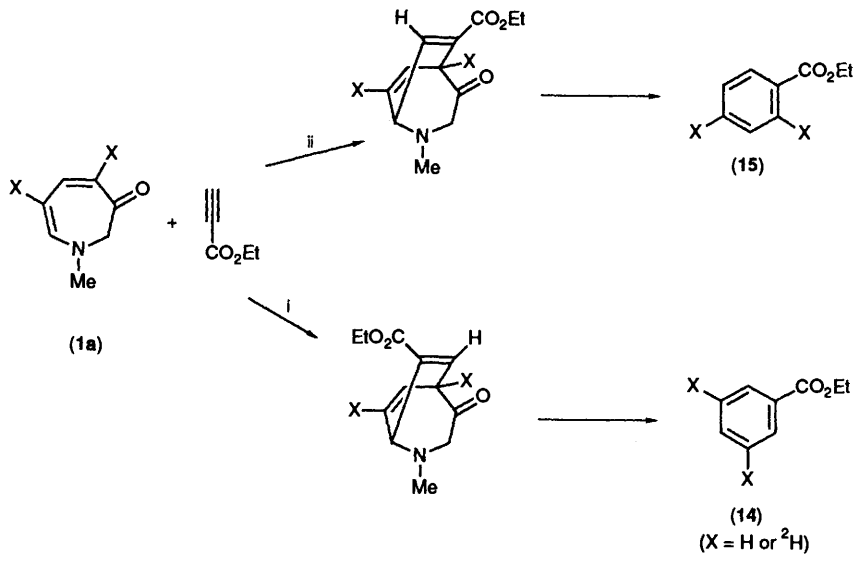
Scheme 2.

reaction is thought to proceed *via* the cycloadduct (**11**) which can then undergo loss of two stable fragments (CO + imine) to yield the aromatic product (Scheme 2). When these reactions were monitored *in situ* by ^{1}H NMR spectroscopy, no significant build-up of aliphatic protons characteristic of the cycloadducts was observed. Though similar results are found with α-pyrone cycloadditions,[13] they are in contrast with those of the isomeric azepin-2-ones [*cf.* (**4**)] which form stable cycloadducts with DMAD;[12] in these cases elimination of the bridge requires formation of an isocyanate and a carbene, which is clearly a much higher energy pathway (Scheme 3).



Scheme 3.

Because the diene (**1**) has an electron-donating *and* an electron-withdrawing substituent it is not clear from qualitative frontier orbital considerations which effect should dominate the coefficients of these orbitals and hence control the regiochemistry of the cycloaddition. The LUMO of electron-deficient dienophiles and the HOMO of electron-rich dienes have the major coefficient at the remote site from the substituent, which leads to the regiochemistry shown in Scheme 4, route i; a



Scheme 4.

stepwise Michael addition followed by collapse of the resulting zwitterion would give a similar result. However, the HOMO of an electron-deficient diene also has its major coefficient at the furthest point from the substituent, which would lead to the pattern of Scheme 4, route ii. In practice, these routes are indistinguishable when X = H, but the deuteriated example (**1a**; X = ^{2}H) was readily prepared by exchange in acid solution[1] and the deuteriated ethyl benzoates (**14**) and (**15**) which would be obtained are distinct, and readily analysed by ^{1}H and ^{2}H NMR spectroscopy. The results were clear cut. Treatment of the deuteriated compound (**1a**) with ethyl propiolate under the standard conditions gave ethyl benzoate whose *ortho*-proton doublet signals (δ_H 8.04) had collapsed to a singlet. A ^{2}H NMR spectrum of the same sample showed a single major peak ($\delta_{^2H}$ 7.46) with no signal at $\delta_{^2H} > 8.0$. Hence the majority of the deuterium label is located at the *meta* position (as required of Scheme 4, route i) and clearly *no* deuterium is located at the *ortho* position (as would be required of Scheme 4, route ii). Although a stepwise reaction cannot be excluded, it appears that the electron-donating group of the diene controls the regiochemistry as well as the Diels–Alder reactivity of the azepinone system. Similar results have been obtained with cycloaddition reactions of 2-pyrones and methyl propiolate.[17]

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, for solutions in [^{2}H]chloroform, unless otherwise stated.

2-Phenyl-2-azabicyclo[3.2.0]*hept-6-en-4-one*.—1-Phenyl-1*H*-azepin-3(2*H*)-one[3] (280 mg, 1.5 mmol) was dissolved in acetone (4 ml) and the solution was irradiated at room temperature, using a 125 W Hg lamp and a quartz vessel. After 48 h, only a trace of starting material remained as shown by TLC [on silica with ethyl acetate–methylene dichloride (50:50) as eluant] and ^{1}H NMR spectroscopy. The solvent was removed under reduced pressure at room temperature and the residue was purified by dry flash column chromatography using methylene dichloride–ethyl acetate mixtures as eluant. The initial eluant was 100% methylene dichloride and the amount of ethyl acetate was increased by 5% every alternate fraction. This gave the product as an orange solid. Attempts to distil or recrystallise the solid led only to recovered azepinone. Thus, the *title compound* was prepared (180 mg, 64%) (Found: M^+, 185.0843. $C_{12}H_{11}NO$ requires M^+, 185.0840); δ_H 7.29 (2 H, dd, ^3J 7.4 and 8.8 Hz), 6.85 (1 H, t, ^3J 7.3 Hz), 6.68 (2 H, d, ^3J 8.9 Hz), 6.60 (1 H, d, ^3J 2.7 Hz), 6.33 (1 H, m), 4.99 (1 H, m), 4.09 (1 H, m), 3.99 (1 H, m) and 3.80 (1 H, m), (further fine coupling is also observed—see Figure 1); δ_C 207.92 (q), 145.84 (q), 141.06, 137.13, 129.29, 118.08, 112.37, 60.23, 55.14, and 54.55; *m/z* 185 (M^+, 18%), 159 (20), 157 (22), 156 (100), 130 (27), 105 (40) and 104 (30).

An investigation of the thermal reversion of the photolytic cyclisation just described was carried out by NMR spectroscopy. A solution of 2-phenyl-2-azabicyclo[3.2.0]hept-6-en-4-one in [$^2H_8$]toluene was kept in a sample tube in the probe of the spectrometer at the required temperature. Anthracene was used as an internal standard and the disappearance of the bicyclic product monitored to allow calculation of rate constants at both 78 and 84.5 °C (see Results and Discussion section).

Reactions of 1H-*Azepin*-3(2H)-*ones with Olefinic Dienophiles*.—(*a*) *Maleic anhydride*. The azepinone[3] (1 mmol) was dissolved in benzene and maleic anhydride (100 mg, 1 mmol) was added. The reaction mixture was stirred at room temperature until reaction was complete as shown by TLC [on silica with ethyl acetate–methylene dichloride (50:50) as eluant]. The reactions were also carried out on a small scale in [$^2H_6$]benzene and monitored by ^{1}H NMR spectroscopy to give an indication of the rate of reaction. The use of other solvents (*e.g.* chloroform or acetonitrile) seemed to have no effect on the reaction. The solvent was removed under reduced pressure to give the Diels–Alder adducts as crystalline solids. The *N*-phenyl compound was purified by recrystallisation, but all attempts to purify the *N*-methyl analogue by recrystallisation resulted in the formation of an insoluble material of undetermined structure. The following 4-*oxo*-2-*azabicyclonon*-8-*ene*-endo-6,7-*dicarboxylic anhydrides* were prepared: 2-*phenyl* (48 h at room temperature) (192 mg, 68%), m.p. 157–158 °C (from methanol) (Found: C, 66.7; H, 4.6; N, 5.05. $C_{16}H_{13}NO_4 \cdot 0.25\ H_2O$ requires C, 66.8; H, 4.7; N, 4.85%) (recrystallises reproducibly as a partial hydrate); δ_H(360 MHz) ([$^2H_6$]-acetone) 7.31 (2 H, apparent t, ^3J 7.5 Hz of d, ^4J 2.0 Hz), 7.02 (2 H, d, ^3J 8.0 Hz), 6.88 (1 H, t, ^3J 7.3 Hz), 6.63 (2 H, m), 5.12 (1 H, m), 4.32 (1 H, d, ^2J 16.0 Hz), 4.09 (1 H, dd, ^3J 8.9 Hz and ^4J 2.4 Hz), 4.02 (1 H, d, ^2J 16.0 Hz), 3.83 (1 H, dd, ^3J 9.0 Hz and ^4J 2.0 Hz) and 3.72 (1 H, m); δ_C 198.84 (q), 170.92 (q), 170.52 (q),

147.57 (q), 130.56, 129.85, 128.73, 119.30, 115.32, 55.92, 54.14, 49.68, 45.05, and 42.11; *m/z* 283 (M^+, 9%), 185 (90), 156 (82), 105 (100), 93 (31) and 77 (48): 2-*methyl* (2 h at room temperature) (180 mg, 81%), m.p. 184–188 °C (decomp.) (crude product) (Found: C, 59.3; H, 5.3; N, 6.6. $C_{11}H_{11}NO_4$ requires C, 59.75; H, 5.0; N, 6.35%); δ_H 6.36 (2 H, m), 4.01 (1 H, d, ^3J 5.8 Hz of apparent t, ^4J 2.1 Hz), 3.79 (1 H, dd, ^3J 9.2 and ^4J 2.3 Hz), 3.60 (1 H, d, ^3J 5.8 Hz of apparent t, ^4J 2.2 Hz), 3.49 (1 H, dd, ^3J 11.4 Hz and ^4J 2.9 Hz), 3.44 (1 H, d, ^2J 15.2 Hz), 3.20 (1 H, d, ^2J 15.2 Hz), and 2.46 (3 H, s); δ_C 199.94 (q), 170.89 (q), 170.64 (q), 130.20, 129.62, 63.09, 57.71, 49.22, 44.78, 44.13 and 42.50; *m/z* 221 (M^+, <1%), 193 (4), 123 (51), and 94 (100).

(*b*) *Tetracyanoethylene.* The 1-phenyl-1*H*-azepin-3(2*H*)-one (30 mg, 0.17 mmol) was dissolved in methanol (1 ml) and a solution of the alkene (21 mg, 0.17 mmol) in methanol (1 ml) was added at room temperature. This gave immediate precipitation of a yellow solid which was practically insoluble in normal organic solvents. A small amount of the material was dissolved in [$^2H_6$]dimethyl sulphoxide to give a bright red solution and the ^1H NMR spectrum which was obtained immediately on making up the solution showed only starting material. It is thought that the solid is a charge transfer complex of the diene and dienophile: (76%), m.p. 120–125 °C (decomp.) (Found: C, 68.2; H, 3.45; N, 22.2. $C_{18}H_{11}N_5O$ requires C, 69.0; H, 3.5; N, 22.35%) (crude product—all attempts at recrystallisation resulted in bright red solutions from which no solid could be obtained); ν_{max} 1615 cm^{-1} (extended amide).

(*c*) *Other olefinic dienophiles.* A number of unsuccessful attempts were made to form adducts with other olefinic dienophiles. These reactions were carried out on a small scale and monitored by ^1H NMR spectroscopy. Heating solutions to the temperature of acetonitrile at reflux (82 °C) for extended periods of time led to apparent decomposition in some cases [1-methylazepinone and ethyl acrylate or 1,2-bis(phenylsulphonyl)ethene, 1-phenylazepinone and 2-(3,3-dimethyltriazen-1-yl)benzoic acid], or to no apparent change [1-phenylazepinone and 2-chloroacrylonitrile, diethyl fumarate, or 1,2-bis(phenylsulphonyl)ethene]. Addition of a Lewis acid catalyst (boron trifluoride–diethyl ether) apparently leads to decomposition of the azepinone.

(*d*) *Reactions of* 1-*methyl*-1H-*azepin*-3(2H)-*one with acetylenic dienophiles.* The azepinone (30 mg, 0.25 mmol) was dissolved in [$^2H_3$]acetonitrile and the appropriate acetylene derivative (0.25 mmol) was added. The reaction was monitored by ^1H NMR spectroscopy and found to give substituted benzene derivatives. Thus, reaction with ethyl propiolate (16 h at reflux) followed by removal of solvent under reduced pressure, and bulb-to-bulb distillation, gave ethyl benzoate (30 mg, 80%), b.p. 98 °C (13 mmHg), δ_C(DEPT, 3π/4) 132.62, 129.35, 128.13, 60.77, and 14.15; GC retention time and ^{13}C NMR spectrum identical with those of an authentic sample. Reaction of the azepinone with dimethyl acetylenedicarboxylate (six days, room temperature) gave dimethyl phthalate (35 mg, 73%), b.p. 110 °C (0.2 mmHg), δ_C(DEPT, 3π/4) 130.92, 128.68 and 52.43; GC retention time and ^{13}C NMR spectrum identical with those of an authentic sample.

4,6-[$^2H_2$]-1-*Methyl*-1H-*azepin*-3(2H)-*one*.—The azepinone (45 mg, 0.36 mmol) was dissolved in [$^2H_4$]methanol (0.4 ml) and [^2H]trifluoroacetic acid (30 μl, 0.38 mmol) was added. After 30 min, the ^1H NMR spectrum indicated that exchange at the 4- and 6-positions was practically complete, [$^2H_2$]water (5 ml) was added and the solution was basified with solid potassium carbonate. The basic solution was extracted with methylene dichloride (4 × 6 ml), the combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to give the title compound (12%).

Reaction of 4,6-[$^2H_2$]-1-*Methyl*-1H-*azepin*-3(2H)-*one with Ethyl Propiolate.*—The small amount of deuteriated azepinone obtained above was dissolved in [^2H]chloroform (0.3 ml) and ethyl propiolate (4.6 μl. 0.05 mmol) was added. The solution was heated at 60 °C and was monitored by ^1H NMR spectroscopy. The reaction yielded ethyl [3,5-$^2H_2$]benzoate; δ_H 8.04 (s), $\delta_{^2H}$ (30 MHz) 7.46 (s).

Pyrolysis of 4-*Oxo*-2-*phenyl*-2-*azabicyclonon*-8-*ene*-endo-6,7-*dicarboxylic anhydride.*—The title compound (20 mg, 0.09 mmol) was subjected to flash vacuum pyrolysis under standard conditions (600 °C, 10^{-3} mmHg, inlet temperature 140 °C, pyrolysis time 15 min). ^1H NMR spectroscopy and GC analysis showed that the pyrolysate consisted of 1-phenyl-1*H*-azepin-3(2*H*)-one and maleic anhydride.

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References

1 Part 3, H. McNab, L. C. Monahan and A. J. Blake, preceding paper.
2 Preliminary communication, H. McNab and L. C. Monahan, *J. Chem. Soc., Chem. Commun.*, 1987, 141.
3 A. J. Blake, H. McNab and L. C. Monahan, *J. Chem. Soc., Perkin Trans. 1*, 1989, 425.
4 E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, 1964, **86**, 950.
5 L. A. Paquette and D. E. Kuhla, *J. Org. Chem.*, 1969, **34**, 2885.
6 J. M. Holovka and P. D. Gardner, *J. Am. Chem. Soc.*, 1967, **89**, 6390.
7 H. Hofmann and B. Meyer, *Tetrahedron Lett.*, 1972, 4597.
8 O. L. Chapman and E. D. Hoganson, *J. Am. Chem. Soc.*, 1964, **86**, 498.
9 L. A. Paquette, *J. Am. Chem. Soc.*, 1964, **86**, 500.
10 E. Vogel, R. Erb, G. Lenz and A. A. Bothner-By, *Liebigs Ann. Chem.*, 1965, **682**, 1.
11 For example, H. Tomisawa and H. Hongo, *Chem. Pharm. Bull.*, 1970, **18**, 941.
12 L. A. Paquette, *J. Org. Chem.*, 1964, **29**, 3447.
13 A. I. Meyers, *Heterocycles in Organic Synthesis*, Wiley, New York, 1974, p. 104, and references therein.
14 For example, G. C. Levy, R. L. Lichter and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd edn., Wiley, New York, 1980, ch. 5.
15 For example, K. E. Wilzbach and D. J. Rausch, *J. Am. Chem. Soc.*, 1970, **92**, 2178.
16 N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 751.
17 J. A. Reed, C. L. Schilling, Jr., R. F. Tarvin, T. A. Rettig and J. K. Stille, *J. Org. Chem.*, 1969, **34**, 2188.

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