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PYRAZOLINO-DIAZEPINES AND HOMODIAZEPINES

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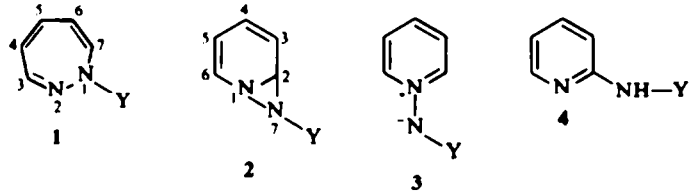
Abstract—1,2-Diazepines 1 undergo various ($2\pi + 4\pi$) as well as ($4\pi + 2\pi$) cycloadditions and lead to bridged adducts 9 and to pyrazolino-diazepines 13 respectively. The elusive 1,7-diazanorcaradiene tautomers 2 could not be trapped through cycloaddition reactions. 1-Pyrazoline 11 as well 2-pyrazoline 13a loose a nitrogen molecule by thermal activation and lead to the expected homodiazepines 16 and 17.

The 7-membered 1,2-diazepines 1 are known to undergo peculiar ring transformations; for example, when heated in various solvents, they isomerize and lead either to 1-iminopyridinium ylides 3 or to 2-aminopyridines 4.[1,2] It is, therefore, reasonable to postulate 1,7-diazanorcaradienes 2 as possible valence tautomers of the 7-membered diazepines 1,[3] thermally induced C(2)–N(7) bond cleavage of 2 would lead to the ylides 3, whereas N(1)–N(7) bond cleavage, followed by a prototropy, would give compounds of type 4.

Pyrazolino-diazepines. Diazepines 1, having electron-attracting substituents in the C-5 position like ethoxycarbonyl, cannot be synthesized photochemically from the corresponding ylides, according to Snieckus.[4] On the contrary 1,4-diethoxycarbonyl-diazepine is easily synthesized[7] and reacts quickly with diazopropane; unfortunately, from the complex reaction mixture, no definite products could be isolated. Therefore we had to turn our attention toward diazepines which are not substituted at the C atoms of the 7-membered



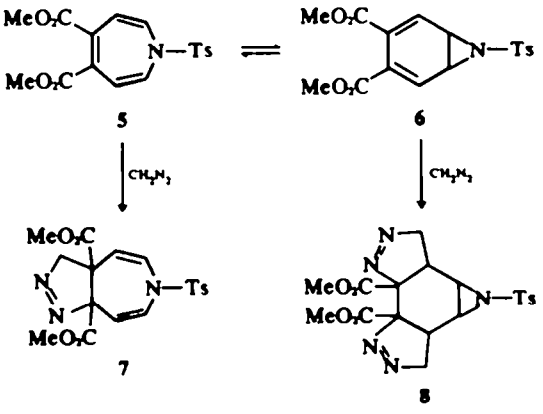
(a) Y = CO_2Et (b) Y = CO_2iPr (c) Y = COC_6H_5 (d) Y = $SO_2C_6H_5$ (e) Y = Ts

On the other hand the bicyclic 1,7-diazanorcaradienes 2 have been postulated, first by us[4] and later on by Sasaki[5] and by Snieckus,[6] either as short-lived intermediates, during the photochemically induced ring expansion of 1-imino-pyridinium ylides 3 toward the isomeric 1,2-diazepines 1, or as valence tautomers of the latter ones. Unfortunately their existence has only been substantiated by indirect chemical evidence.[1,2]

Prinzbach *et al.* demonstrated the existence of a valence tautomeric equilibrium between N-tosyl azepine 5 and 7-azanorcaradiene 6: reaction with diazomethane gave the tetracyclic adduct 8 as well as the unstable pyrazoline 7[3c] (Scheme 1). Assuming that 1,2-diazepines 1 exist in valence tautomeric equilibrium with 1,7-diazanorcaradienes 2, it seemed desirable to freeze both isomers by using a similar approach. Furthermore both tautomers were expected to react with diazoalkanes in order to give 1-pyrazoline derivatives which, by thermal or by photochemical activation, could yield homodiazepines.

ring skeleton and which, for that reason, have no activated double bonds.

Tetracyanoethylene[3] as well as 4-phenyl-1,2,4-triazoline-3,5-dione react easily with 1,2-diazepines



SCHEME 1.

but only adducts of these 7-membered tautomers are isolated in moderate to good yields;[8] for example 1-ethoxycarbonyl-1,2-diazepine **1a** yields, after reaction with the triazoline reagent, the crystalline adduct **9a** (Table 2).

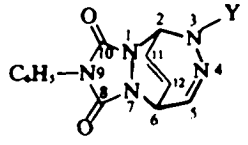
Diazomethane adds slowly to 1-benzenesulfonyldiazepine **1d**, yielding the crystalline adduct **10**, the structure of which could be deduced from ^{1}H NMR. The UV spectrum of **10** shows an extensive conjugation at λ_{max} 337 nm (ϵ 9,900). From this reaction one would have expected the formation of a 1-pyrazoline adduct; obviously isomerisation to the more stable, and to a higher degree conjugated, 2-pyrazoline **10** occured in a second step. Other diazepines, which bear substituents at N-1 with less electron-attracting power, do not react with diazomethane. Therefore the more reactive diazopropane had to be used.[9]

In order to achieve the synthesis of a stable 1-pyrazoline adduct, diazopropane in reaction with 1-ethoxycarbonyl-3,5-dimethyldiazepine yielded a colourless adduct, m.p. 81–83°, which was a 1-pyrazoline derivative, as shown by UV spectroscopy (λ_{max} 342 nm (ϵ 320)]. The presence of a Me substituent in the C-1 position obviously prevented isomerisation of the azo-double bond. NMR data support the proposed structure **11**.

cycloaddition of diazoalkanes yielding the adducts we obtained. Nevertheless, the N-1 sp^2 atom[11] is also part of an urethane, amide or sulfamide moiety, and is therefore less prone to donate its "free" electron pair to the butadiene part. Probably the Δ^4 double bond is only slightly activated in such a way as to obtain a partial negative charge at the C-4 position, although one may argue that the Δ^2 imine double bond should also have an electron-withdrawing effect upon the Δ^4 double bond. The X-ray data indicate that this is not the case: the imine double bond is not conjugated with either the butadiene or the urethane moieties.[11]

In conclusion we recognized that our initial goal had not been achieved: neither TCNE, nor phenyl-triazolinedione, nor diazoalkanes trap the highly elusive 1,7-diazanorcaradiene tautomers **2**. If there is an equilibrium between tautomers of type **1** and **2**, it is predominantly shifted toward the 7-membered ring.

Homodiazepines. Since NMR experiments, determined at various temperatures, did not establish the presence of a diaza-norcaradiene tautomer, we looked for a similar Cope rearrangement between type **14** homodiazepines and their isomeric diaziridines **15**[3] (Scheme 2). An obvious approach to the synthesis of such homodiazepines could be



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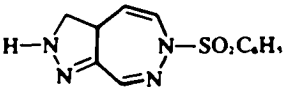

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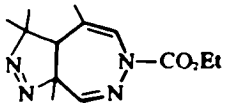

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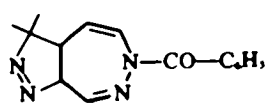

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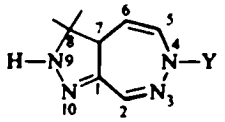

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Diazepines, having no substituents other than hydrogen in the C-4 position, led directly to 2-pyrazoline adducts with diazopropane, in all but one instance: 1-benzoyl-1,2-diazepine **1c** gave the crystalline adduct **12**, m.p. 86–89°, the structure of which depends upon its NMR spectrum (Fig 1 and Table 3). In solution adduct **12** isomerised slowly to the more stable 2-pyrazoline **13c** (Fig 1). The other unsubstituted diazepines gave 2-pyrazoline derivatives **13** in fair yields (Table 4). Alternative structures for the diazopropane adducts were discarded on the basis of NMR and UV spectroscopy; furthermore an X-ray diagram, measured and calculated by Allmann[10] with the lead tetraacetate oxidation product of **13a**, provided definite proof for the proposed structures **13** (*vide infra*). The Δ^4 and Δ^6 diazepine double bonds are part of a dienamine moiety; one would therefore expect a regiospecific

via nitrogen molecule expulsion from 1-pyrazoline derivatives, either by thermal[12] or by photosensitized activation.[13] UV irradiation of xanthone in the presence of pyrazoline **11** yielded, albeit in low yield, the expected homodiazepine **16**; pyrolysis of **11** gave, within minutes and in 78% yield, the same compound **16**. The NMR spectrum is in good agreement with the proposed structure, which is therefore 1,6,8,8-tetraméthyl-4-ethoxycarbonyl-3,4-diazabicyclo[5.1.0]2,5-octadiene. In a similar fashion even 2-pyrazolines could yield the corresponding homodiazepines. Compound **13a**, when pyrolyzed at 170° gave homodiazepine **17** in 35% yield. Again the NMR spectrum is in agreement with the presence of this only tautomer, since three vinylic protons show up, whereas four such protons would be present in the other Cope tautomer. NMR measurements, performed at various temperatures with

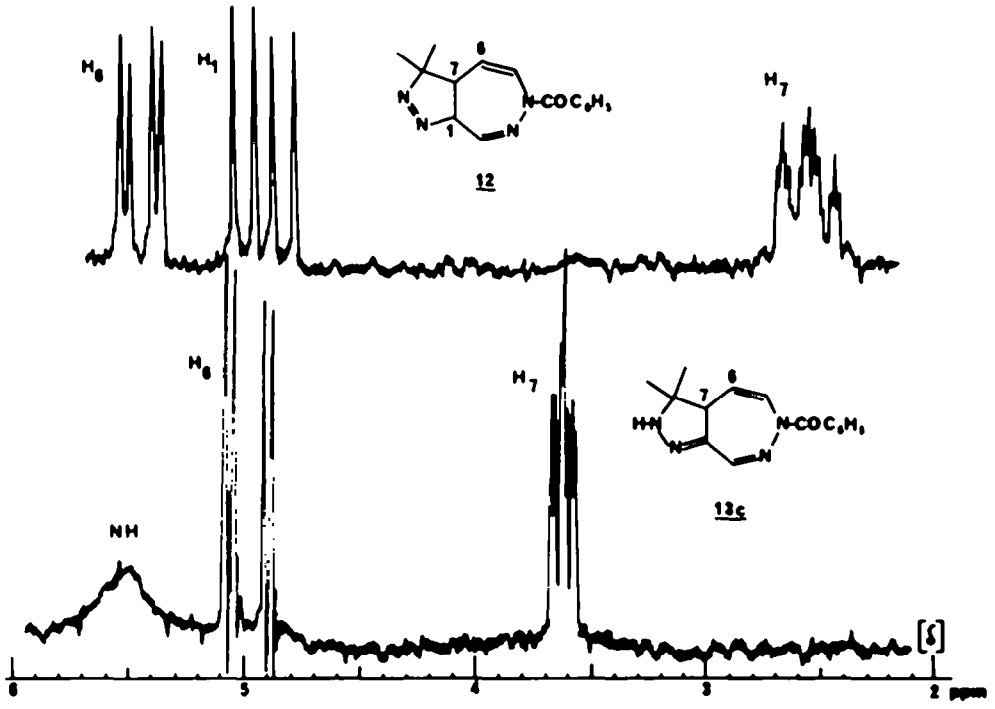
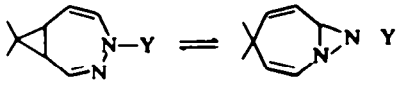


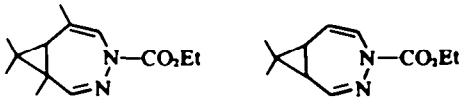
Fig 1.

homodiazepines **16** and **17**, do not indicate the presence of a second tautomer. From these observations we conclude that diaziridines of type **15** do not form easily—if at all—from the corresponding diazepines.



14 **15**

SCHEME 2



16 **17**

Abnormal lead tetraacetate oxidation of pyrazolino-diazepine **13a**. The observation that even 2-pyrazolines like **13a** pyrolyse, although in low yield, to cyclopropanes, favours a prototropic equilibrium between 1- and 2-pyrazolines. The latter obviously predominate, since all double bonds are conjugated, a situation which stabilizes these compounds. Nevertheless we planned to shift the $\Delta^{1\text{-}10}$ double bond of compounds **13** back to the initial Δ^{8} position. Such double bond migration had already been achieved with (1-H)2-pyrazolines by oxidation with lead tetraacetate;[12] for example 2-pyrazoline **18** is oxidized by $Pb(OAc)_4$ into 3 - acetoxy - 1 - pyrazoline **19**.[14] Lead tetraacetate oxidation of compound **13a** gave a 40% yield of a colourless acetoxy derivative, m.p. 129–131°, whose gross formula is isomeric with the expected product **20**. The ^1H NMR spectrum immediately ruled out structure **20**, since only one vinylic proton shows up. The combination of ^1H and ^{13}C NMR, as well as X-ray analysis, indicate structure **21** which is therefore 4 - ethoxycarbonyl - 5 - acetoxy - 8,8 - dimethyl - 3,4,9,10 - tetraazatricyclo[5.3.0.0^{1,6}]2,9-decadiene, with the stereostructure shown in Fig 2.[10]

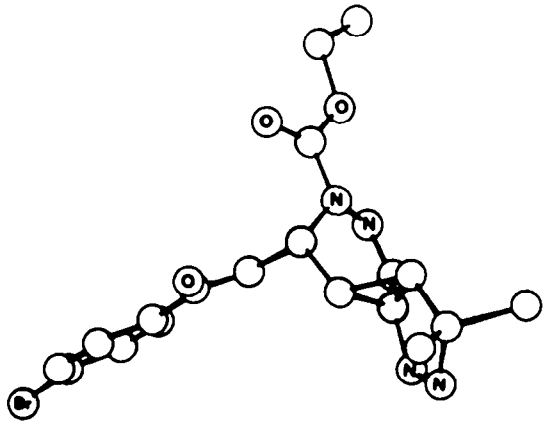
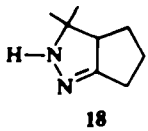


Fig 2.



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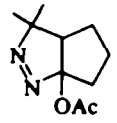

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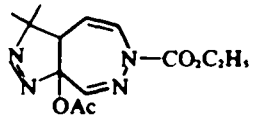

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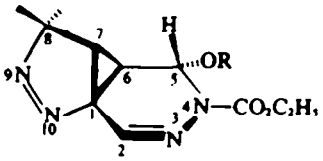
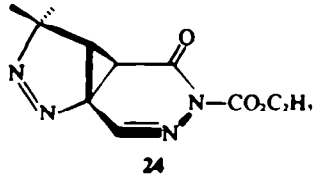


21: R = Ac
22: R = H
23: R = COC_6H_4Br



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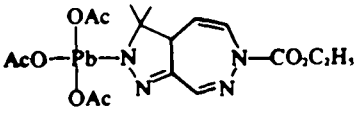

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Radical or cation

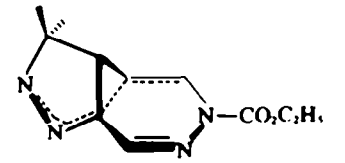

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Table 1. NMR spectral data of the acetate 21, the parabromobenzoate 23 and of carbonyl derivative 24; chemical shifts in ppm measured in CDCl, at 60 MHz vs TMS; coupling constants in Hz

	H-2	H-5	H-6	H-7	Me-8
21	δ 8·28	δ 7·00 $J_{5,6}$ = 0·5 $J_{5,7}$ = 0·3	δ 1·94 $J_{6,7}$ = 5·0 $J_{6,2}$ = 0·5 $J_{6,2}$ = 0·3	δ 2·68 $J_{7,6}$ = 5·0 $J_{7,5}$ = 0·3	δ 1·44 δ 1·57
23	δ 8·33	δ 7·26 $J_{5,6}$ = 1	δ 1·86 $J_{6,7}$ = 4 $J_{6,2}$ = 1 $J_{6,2}$ = 0·3	δ 2·45 $J_{7,6}$ = 4	δ 1·38 δ 1·52
24	δ 8·05		δ 1·80 $J_{6,7}$ = 4·5 $J_{6,2}$ = 0·5	δ 2·30 $J_{7,6}$ = 4·5	δ 1·45 δ 1·57

Saponification of the acetate 21 gave the stable hydroxy derivative 22 which was easily oxidised with Jones' reagent to compound 24; X-ray analysis was performed with the parabromobenzoate 23.[10] The main features of the NMR spectra of the hemiaminal 22 are as follows: ^1H *NMR* ($CDCl_3$): H-2 (δ 8·25 ppm; s); H-5 (δ 6·08 ppm; J = 1·0 Hz); H-6 (δ 1·69 ppm; J = 5·0; 1·0 Hz) and H-7 (δ 2·34 ppm; J = 5·0 Hz); Me-8 (δ 1·44 and 1·57 ppm); ^{13}C *NMR* ($CDCl_3$): two sp^2 carbon atoms are present at δ 146·9 (C-2) and δ 155·6 ppm (C═O); with "off resonance" measurements, two quaternary carbon atoms show up at 71·2 ppm (C-1) and at δ 88·8 ppm (C-8); tertiary carbon atoms appear at δ 146·9 ppm (C-2), δ 70·8 ppm (C-5), δ 41·4 ppm (C-6) and δ 33·9 ppm (C-7). The magnitude for the C-H coupling constants (J higher than 160 Hz), which appear at 33·9 and 41·4 ppm are clearcut evidence for the presence of a cyclopropane.[15]

The vinylic $Pb(OAc)_4$ oxidations of 2-pyrazolines have not been reported. In the synthesis of the acetoxy derivative 21, probably the first step is for-

mation, of the labile lead-triacetate complex **25**; homolytic or heterolytic Pb-N bond cleavage[16] in a second step should yield the highly delocalized radical or cationic species of type **26**. Acetic acid action on **26** would eventually give the acetoxy derivative **21**. A concerted acetolysis of the lead complex **25** can be ruled out: such a stereoelectronically controlled process would result in the wrong configuration at C-5.

EXPERIMENTAL

Microanalyses were performed by the Service Central de Microanalyse du CNRS at Lyon and Strasbourg. M.ps were measured on a LEITZ apparatus and are uncorrected. IR and UV spectra were determined with BECKMAN IR-20-A and DB spectrophotometers respectively. ^{1}H NMR spectra were obtained with Varian A-60-A, T-60 and HA-100 spectrometers in deuterated solvents using TMS as an internal standard (s = singlet; d = doublet; t = triplet; q = quadruplet; m = multiplet). ^{13}C NMR spectra were recorded with a Varian XL 100/5 apparatus. Mass spectroscopic determinations were performed with an LKB-9000-S apparatus. Column, thin and thick layer chromatographies were carried out with silicic acid from Merck (Darmstadt). Solvents are reagent grade and were distilled before use. Photochemical reactions were conducted in a Pyrex vessel and cooled internally to 10–20° by a double-walled Pyrex finger.

Diels-Alder reactions of 1,2-*diazepines* **1** *with* 4 - *phenyl* - 1,2,4 - *triazoline* - 3,5 - *dione*

The general procedure is described for the preparation of 3 - *Isopropoxycarbonyl* - 9 - *phenyl* - 1,3,4,7,9 - *pentaaza* - *tricyclo*[5.3.2^{2,6}.0]*dodeca* - 4,11 - *diene* - 8,10 - *dione* **9b**. A soln of **1b** (725 mg; 4 mmoles) in methylene chloride (110 ml) was added dropwise, at 0° under N_2, to a methylene chloride soln of triazoline dione (700 mg; 4 mmoles in 15 ml). After continuous stirring at 0° for 4 h, the red colour of triazoline dione disappeared; the solvent removed *in vacuo*, the residue dissolved in MeOH and treated at reflux temp with charcoal. The resulting filtrate was evaporated to dryness *in vacuo* and the remaining solid material recrystallized twice from acetone/ether 4/1 to yield 972 mg of **9b** (69%), m.p. 184–185° dec. (colourless crystals); IR (KBr) ν (C=O) 1780 and 1725 cm^{-1}; UV (MeOH) λ_{max} 221 nm (ϵ 17,700), shoulder at 266 nm; MS *m/e* 335 (M$^+$), *m/e* 180 (retro-Diels peak) (Found: C, 57·5; H, 5·0; N, 19·4. Calcd for $C_{17}H_{17}O_4N_5$: C, 57·46; H, 4·82; N, 19·71%).

3 - *Ethoxycarbonyl* - 9 - *phenyl* - 1,3,4,7,9 - *pentaaza* - *tricyclo*[5.3.2.^{2,6}0]*dodeca* - 4,11 - *diene* - 8,10 - *dione* **9a**. The same procedure was applied to the synthesis of **9a**; from 1 g **1a**, 1·6 g of the adduct (yield: 78%), m.p. 212–213° dec, was obtained as colourless crystals; IR (KBr) ν (C=O) 1775 and 1725 cm^{-1}; UV (MeOH) λ_{max} 221 nm (ϵ 17,600), shoulder at 264 nm; MS *m/e* 341 (M$^+$), *m/e* 166 (retro-Diels peak). (Found: C, 56·1; H, 4·4; N, 20·5. Calcd. for $C_{16}H_{15}O_4N_5$: C, 56·30; H, 4·43; N, 20·52%).

3 - *Benzenesulfonyl* - 9 - *phenyl* - 1,3,4,7,9 - *pentaaza* - *tricyclo*[5.3.2^{2,6}.0]*dodeca* - 4,11 - *diene* - 8,10 - *dione* **9d**. Starting with 2·34 g of **1d**, 1·23 g of **9d** (33% yield); m.p. 150° (dec) was obtained as unstable colourless crystals; IR (KBr) ν (C=O) 1775 cm^{-1}, ν (S=O) 1370 and 1170 cm^{-1}; UV (MeOH) λ_{max} 215 nm (ϵ 18,400), shoulder at 260 nm; MS *m/e* 409 (M$^+$), *m/e* 234 (retro-Diels peak). No elementary microanalysis could be obtained (unstable crystals).

3 - *Tosyl* - 9 - *phenyl* - 1,3,4,7,9 - *pentaaza* - *tricyclo*[5.3.2^{2,6}.0]*dodeca* - 4,11 - *diene* - 8,10 - *dione* **9e**. From 1·3 g **1e** 865 mg of **9e** (41% yield); m.p. 212–213° (dec) was obtained as colourless crystals; IR (KBr) ν (C=O) 1780 cm^{-1}, ν (S=O) 1370 and 1175 cm^{-1}; UV (MeOH) λ_{max} 222 nm (ϵ 18,400), shoulder at 240 nm; MS *m/e* 423 (M$^+$), *m/e* 248 (retro-Diels peak). No elementary microanalysis could be obtained (unstable crystals).

Tentative 1,3 *dipolar cycloadditions of diazomethane with diazepines* **1**.

Diazomethane is usually inert with diazepines **1**. For example 1 - ethoxycarbonyl - 1,2 - diazepines **1a** in diethyl ether solution did not react with diazomethane over a period of 2 weeks at temps ranging from − 30° to + 35°; the starting diazepine was quantitatively recovered. Only 1-benzenesulfonyl - 1,2 - diazepine reacted with diazomethane.

Table 2. NMR spectra of triazoline adducts with 1,2-diazepines; chemical shifts expressed in ppm relative to T.M.S.; coupling constants in Hz

	H-2	H-5	H-12	H-11	H-6
9a (CDCl$_3$) 60 MHz	δ 7·11 $J_{2,11}$ = 6·8 $J_{2,12}$ = 1·5	δ 7·05 $J_{5,6}$ = 5·4 $J_{5,12}$ = 0·6	δ 6·47 $J_{12,11}$ = 8·5 $J_{12,6}$ = 6·3 $J_{12,2}$ = 1·5 $J_{12,5}$ = 0·6	δ 6·14 $J_{11,12}$ = 8·5 $J_{11,2}$ = 6·8 $J_{11,6}$ = 1·8	δ 4·95 $J_{6,12}$ = 6·3 $J_{6,5}$ = 5·4 $J_{6,11}$ = 1·8
9b (C_6D_6,C_5D_5N,8/2) 100 MHz	δ 6·14 J = 6·8; 1·4	δ 5·58 J = 5·4; 0·6	δ 4·87 J = 8·5; 6·3; 1·4; 0·6	δ 4·63 J = 8·5; 6·8; 1·8	δ 3·90 J = 6·3; 5·4 1·8
9d DMSO-d-6 60 MHz	δ 7·3 masked by aromatic protons	δ 6·96 J = 5·5; 0·7	δ 6·62 J = 8·5; 6·2; 1·5; 0·7	δ 6·36 J = 8·5; 7·0; 1·8	δ 5·07 J = 6·2; 5·5; 1·8
9e DMSO-d-6 60 MHz	δ 7·3 masked by aromatic protons	δ 6·92 J = 5·5; 0·8	δ 6·67 J = 8·5; 6·2; 1·5; 0·8	δ 6·43 J = 8·5; 7·0; 1·8	δ 5·18 J = 6·2; 5·5; 1·8

4 - *Benzenesulfonyl* - 3,4,9,10 - *tetraza* - *bicyclo*[5.3.0]*deca* - 2,5,10 - *triene* **10**. A soln of **1d** (2 g; 8·6 mmoles)[a] and excess diazomethane (1·2 g; 28 mmoles) in 20 ml diethyl-ether was left standing at − 30°; after 10 hr the starting diazepine had disappeared as shown by TLC. The solvent was removed *in vacuo* and the remaining products are crystallized from benzene/hexane 1/1: adduct **10** (1·8 g; 76% yield) was obtained as colourless crystals which proved to be stable only when kept at 0° under N_2 in a drybox; mp 148–149° (dec); IR (KBr) ν (N—H) 3320 cm^{-1}; ν (S═O) 1360 and 1170 cm^{-1}; UV ($CHCl_3$) λ_{max} 337 nm (ϵ 9,900); MS *m/e* 276 (M^+). NMR ($CHCl_3$): H-2 (δ 7·48 ppm; s), H-5 (δ 6·67 ppm; J = 8·3 and 2·8 Hz), H-6 (δ 5·01 ppm; J = 8·3 and 2·3 Hz), H-7 (δ 4·32 ppm; J = 11·5: 10·5; 2·8 and 2·3 Hz), H-8 (δ 3·84 ppm; J = 9·0 and 10·5 Hz) H-8' (δ 3·25 ppm; J = 9·0 and 11·5 Hz) and H-9 (δ 5·35; s). No elementary microanalysis could be performed (unstable product).

1,3-*Dipolar cycloadditions of diazopropane (DAP) to* 1,2-*diazepines* **1**

Synthesis of diazopropane (DAP). The highly unstable diazopropane (DAP) was synthesized according to the elaborate Neumann procedure:[9] acetone-hydrazone (15 g) was oxidized with mercuric oxide (50 g) in ethylbenzene, the DAP which formed being continuously distilled under reduced pressure along with ethylbenzene into a trap maintained at − 80°. About 15 ml of a red DAP soln in ethylbenzene was obtained and diluted with 20 ml deep-cooled diethylether.

All operations were conducted at − 80°; the DAP soln was stored in the dark at dry ice temp.

Synthesis of 4- - *ethoxycarbonyl* - 1,6,8,8 - *tetramethyl* - 3,4,9,10 - *tetraza* - *bicyclo*[5.3.0]*deca* - 2,5,9 - *triene* **11**. An ethylbenzene/diethylether soln of DAP (60 ml) was added at − 80° to 2 g ethoxycarbonyl - 4,6 - dimethyl - 1,2 - diazepine[6] in 20 ml diethylether. After being kept for 8 days at − 78° in the dark, the soln was evaporated *in vacuo* to dryness; the products were chromatographed over silicic acid thick layer plates with ethyl acetate/cyclohexane 2/8. Besides minor amounts of an unknown product, the structure of which was not investigated, unreacted diazepine (1·3 g) and adduct **11** (0·5 g; 18% yield), m.p. 81–83° was isolated and recrystallized from benzene; IR ($CHCl_3$) ν (C═O) 1710 cm^{-1}, ν (N═N) 1505 cm^{-1}; UV ($CHCl_3$) λ_{max} 342 nm (ϵ 320), 285 nm (ϵ 2,400) and 243 nm (ϵ 7,700); NMR ($CDCl_3$): H-2 (δ 6·94 ppm; s); H-5 (δ 6·92 ppm; J = 1·3 and 0·8 Hz), H-7 (δ 2·15 ppm; J = 0·8 and 0·6 Hz); four signals for Me groups at δ 1·80 (J = 1·3 Hz); 1·74; 1·69 and 1·04 ppm. (Found: C, 59·0; H, 7·5; N, 21·0. Calcd. for $C_{13}H_{20}N_4O_2$: C, 59·07; H, 7·58; N, 21·20%).

4 - *Benzoyl* - 8,8 - *dimethyl* - 3,4,9,10 - *tetraza* - *bicyclo*[5.3.0]*deca* - 2,5,9 - *triene* **12**. A DAP soln (30 ml) was added at − 80° to **1c** (2 g; 10 mmoles) in 25 ml dry ether. After 20 h at − 80° in the dark, the soln was slowly brought to room temp and evaporated *in vacuo* to dryness yielding directly the pure, crystalline but unstable 1-pyrazoline **12** (1·2 g; 44% yield), m.p. 86–89° dec; IR ($CHCl_3$) ν (C═O) 1675 cm^{-1}; MS *m/e* 268 (M^+). No elementary microanalysis could be determined (unstable product).

4 - *Benzoyl* - 8,8 - *dimethyl* - 3,4,9,10 - *tetraza*-*bicyclo*[5.3.0]*deca* - 2,5,10 - *triene* **13c**. A chloroform soln (10 ml) of **12** (1·1 g) kept at 35° for 2 h led to the formation of **13c** according to NMR spectroscopy (Fig 1). After evaporation of the solvent *in vacuo* the remaining product was chromatographed over 100 g silicic acid with ethyl acetate/cyclohexane 3/7. A pale yellow oil was obtained (880 mg) which was distilled with slight decomposition at 50° under $2 \cdot 10^{-3}$ mm and identified as **13c**; IR ($CHCl_3$) ν (N—H) 3370 cm^{-1}; ν (C═O) 1675 cm^{-1}; UV ($CHCl_3$) λ_{max} 328 nm (ϵ 11,100); MS *m/e* 268 (M^+). No elementary microanalysis could be performed due to the unstability of the product.

4 - *Ethoxycarbonyl* - 8,8 - *dimethyl* - 3,4,9,10 - *tetraza* - *bicyclo*[5.3.0]*deca* - 2,5,10 - *triene* **13a**. A DAP soln (30 ml) was added at − 80° to **1a** (1·66 g; 10 mmoles) in 20 ml dry ether. After 15 h at − 80° in the dark, the soln was slowly brought to room temp and evaporated *in vacuo*; the adduct **13a** (1·9 g; 80% yield) was directly recrystallized from benzene, m.p. 135–137° as colourless crystals; IR ($CHCl_3$) ν (N—H) 3340 cm^{-1}, ν (C═O) 1720 cm^{-1}; UV ($CHCl_3$) λ_{max} 328 nm (ϵ 11,200) and 244 mm (ϵ 9,500); MS *m/e* 236 (M^+). (Found: C, 55·9, H, 6·7; N, 23·8. Calcd. for $C_{11}H_{16}N_4O_2$: C, 55·93; H, 6·78; N, 23·73%).

4 - *Isopropoxycarbonyl* - 8,8 - *dimethyl* - 3,4,9,10 - *tetra* - *bicyclo*[5.3.0]*deca* - 2,5,10 - *triene* **13b**. A DAP soln (30 ml) was added at − 80° to **1b** (2 g; 11 mmoles) in 20 ml dry ether. After 15 h at − 80°, the soln was slowly brought to room temp and evaporated *in vacuo*. Adduct **13b** (1·8 g; 61% yield) was recrystallized from benzene, m.p. 136–138° as colourless crystals; IR ($CHCl_3$) ν (N—H) 3370 cm^{-1}, ν (C═O) 1720 cm^{-1}; UV ($CHCl_3$) λ_{max} 327 nm (ϵ 11,900), 242 nm (ϵ 10,400) MS *m/e* 250 (M^+). (Found: C, 57·8; H, 7·1; N, 22·6. Calcd. for $C_{12}H_{18}N_4O_2$: C, 57·58; H, 7·25; N, 22·39%).

4 - *Benzenesulfonyl* - 8,8 - *dimethyl* - 3,4,9,10 - *tetraza* - *bicyclo*[5.3.0]*deca* - 2,5,10 - *triene* **13d**. A DAP soln (40 ml) was added at − 80° to **1d** (2 g; 8·4 mmoles) in 20 ml dry ether. After 3 h at − 80°, the starting material had disappeared, the soln was evaporated *in vacuo* and the mixture

Table 3. NMR spectral data measured with 1-pyrazoline **12** and with 2-pyrazoline **13c** in $CDCl_3$; chemical shifts expressed in ppm relative to TMS, coupling constants in H_z

	H-1	H-2	H-5	H-6	H-7	H-9	Me-8
12	δ 4·96 $J_{1,2}$ = 10·5 $J_{1,7}$ = 6·0	δ 7·4 masked by aromatic protons	δ 7·5 $J_{5,6}$ = 8·0 $J_{5,7}$ = 1·0	δ 5·49 $J_{6,5}$ = 8·0 $J_{6,7}$ = 2·5	δ 2·59 $J_{7,1}$ = 6·0 $J_{7,6}$ = 2·5 $J_{7,5} = J_{7,2}$ = 1·0		δ 1·68 δ 1·00
13c		δ 7·4 masked by aromatic protons	δ 7·4 masked by aromatic protons	δ 5·01 $J_{6,5}$ = 10·0 $J_{6,7}$ = 2·5	δ 3·64 $J_{7,6}$ = 2·5 $J_{7,5}$ = 1·5 $J_{7,2}$ = 1·0	δ 5·55	δ 1·38 δ 1·02

chromatographed over a silicic acid column with ethyl acetate/cyclohexane 3/7. Adduct **13d** was isolated as a pale yellow and unstable oil (1·3 g; 50% yield) which was purified by distillation at 40° under 10^{-2} mm; IR ($CHCl_3$) ν (N—H) 3400 cm^{-1}, ν (S═O) 1360 and 1172 cm^{-1}; UV ($CHCl_3$) λ_{max} 328 nm (ϵ 11,100); MS *m/e* 304 (M^+). No elementary microanalysis could be performed (unstable product).

4 - *Tosyl* - 8,8 - *dimethyl* - 3,4,9,10 - *tetraza* - *bicyclo*[5.3.0]*deca* - 2,5,10 - *triene* **13e**. A DAP soln (40 ml) was added at −80° to **1e** (2 g; 8 mmoles) in 20 ml methylene chloride and 10 ml ether. After 2 days at −80° the soln is brought to room temp and evaporated *in vacuo*. Direct recrystallization of the product yielded the adduct **13e** as colourless crystals (1·25 g; 49%), m.p. 148–149°; IR ($CHCl_3$) ν (N—H) 3360 cm^{-1}, ν (S═O) 1360 and 1172 cm^{-1}; UV ($CHCl_3$) λ_{max} 328 nm (ϵ 11,000); MS *m/e* 318 (M^+). (Found: C, 56·7; H, 5·8; N, 17·3. Calcd. for $C_{15}H_{18}N_4O_2S$: C, 56·59; H, 5·70; N, 17·58%).

4 - *Ethoxycarbonyl* - 5 - *acetoxy* - 8,8 - *dimethyl* - 3,4,9,10 - *tetrazatricyclo*[5.3.0.$0^{1,4}$]*deca* - 2,9 - *diene* **21**. To a stirred methylene chloride soln (30 ml) of **13a** (800 mg; 3·4 mmoles) at 5°, a soln of lead tetracetate (2 g) in 15 ml methylene chloride was added dropwise over a period of 30 min. After one additional h at room temp the mixture was poured over iced water. The combined methylene chloride extracts were neutralised, dried and evaporated to dryness; the resulting mixture was chromatographed over a 100 g silicic acid column with ethyl acetate/cyclohexane 3/7. Acetate **21** was obtained (400 mg; 40% yield) as colourless crystals, m.p. 129–131°; IR (KBr) ν (C—H) 3060 cm^{-1} (cyclopropyl hydrogens), ν C═O) 1750 and 1730 cm^{-1}, ν (N═N) 1545 cm^{-1}; UV ($CHCl_3$) λ_{max} 327 nm (ϵ 410), 246 nm (ϵ 5,900); MS *m/e* 294 (M^+). (Found: C, 53·6; H, 6·3; N, 19·1. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53·05; H, 6·16; N, 19·04%).

4 - *Ethoxycarbonyl* - 5 - *hydroxy* - 8,8 - *dimethyl* - 3,4,9,10 - *tetrazatricyclo*[5.3.0.$0^{1,4}$]*deca* - 2,9 - *diene* **22**. A soln of **21** (1 g; 3·4 mmoles), in 50 ml abs EtOH, was treated with one equiv of NaOEt (70 mg Na in 15 ml EtOH) for 30 min at room temp. After neutralization with HCl, dilution with water and several extractions of the soln with methylene chloride, a residue which was chromatographed over a column of 70 g silicic acid with ethyl acetate/cyclohexane 5/5 was obtained. Compound **22** (320 mg; 37% yield) was isolated as pale yellow crystals, m.p. 108–109°; IR (KBr), ν (O—H) 3460 cm^{-1}, ν (C—H) 3060 cm^{-1} (cyclopropyl hydrogens), ν (C═O) 1730 cm^{-1}, ν (C═N) 1620 and ν (N═N) 1520 cm^{-1}; UV ($CHCl_3$) λ_{max} 329 nm (ϵ 400) and 248 nm (ϵ 6,000); MS *m/e* 252 (M^+). (Found: C, 52·3; H, 6·4; N, 20·9. Calcd. for $C_{11}H_{16}O_4N_4$: C, 52·37; H, 6·39; N, 22·21%).

Table 4. NMR data of the pyrazolino-diazepines **13** measured at 60 MHz; chemical shifts expressed in ppm relative to TMS, coupling constants in Hz

	H-2	H-5	H-6	H-7	H-9	Me-8
13a	δ 7·55	δ 7·07 $J_{5,6}$ = 10 $J_{5,7}$ = 3·5	δ 5·90 $J_{6,7}$ = 10 $J_{6,9}$ = 2·8	δ 4·62 $J_{7,6}$ = 2·8 $J_{7,5}$ = 3·5	δ 6·88	δ 1·38; 1·02
13b	δ 7·60	δ 7·18 J = 9·8; 3·0	δ 4·98 J = 9·8; 2·5	δ 3·72 J = 2·5; 3·0	δ 6·0	δ 1·45; 1·11
13d	δ 7·50	δ 7·03 J = 9·8; 3·0	δ 4·85 J = 9·8; 2·5	δ 3·60 J = 2·5; 3·0	δ 5·80	δ 1·34; 0·95
13e	δ 7·48	7·08 J = 9·5; 3·3	δ 4·88 J = 9·5; 2·8	δ 3·64 J = 2·8; 3·3	δ 5·77	δ 1·35; 0·97

Syntheses of homodiazepines

4 - *Ethoxycarbonyl* - 1,6,8,8 - *tetramethyl* - 3,4 - *diaza* - *bicyclo*[5.1.0]*octa* - 2,5 - *diene* **16**. A. *Through pyrolysis.* A tube, containing 200 mg of **11** was flushed with N_2 and heated up to 180° for 1 min, after which time no more gas evolution was observed. The pale yellow melt was cooled and chromatographed over silicic acid thick layer plates with ethyl acetate/cyclohexane 3/7; **16** was obtained as colourless crystals (140 mg; 78% yield), m.p. 65–67°; IR ($CHCl_3$) ν (C═O) 1705 cm^{-1}; UV ($CHCl_3$) λ_{max} 266 nm (ϵ 3,000) and 242 nm (ϵ 5,600); MS *m/e* 236 (M^+). NMR ($CDCl_3$): H-2 (δ 6·85 ppm; J = 1·8 Hz); H-5 (δ 6·60 ppm; J = 2·5; 0·6 Hz); Me-6 (δ 1·71 ppm; J = 0·6 Hz); H-7 (δ 1·30 ppm; J = 2·5; 1·8); Me-1 (δ 1·27 ppm); 2 Me-8 at δ 1·27 and 1·0 ppm. (Found: C, 66·0; H, 8·6; N, 12·0. Calcd. for $C_{13}H_{20}N_2O_2$: C, 66·07; H, 8·53; N, 11·86%).

B. *Through sensitized photolysis.* A 100 ml benzene soln of **11** (200 mg) and xanthone, [300 mg; λ_{max} 340 nm (ϵ 9,800)] was irradiated with a Philips HPK 125 mercury lamp through Pyrex glass. After 24 h the mixture was chromatographed over silicic acid thick layer plates with ethyl acetate/cyclohexane 3/7; homodiazepine **16**, m.p. 65–67° is isolated in 5% yield only (10 mg).

4 - *Ethoxycarbonyl* - 8,8 - *dimethyl* - 3,4 - *diaza* - *bicyclo*[5.1.0]*octa* - 2,5 - *diene* **17**. A tube, containing **13a** (200 mg) was flushed with N_2 and heated to 170° for about 6 min, after which time gas evolution ceased. The mixture was chromatographed over silicic acid thick layer plates with ethyl acetate/cyclohexane 3/7. Homodiazepine **17** was obtained (80 mg; 35% yield) as a colourless and stable oil, IR ($CHCl_3$) ν (C═O) 1710 cm^{-1}; UV (MeOH) λ_{max} 259 nm (ϵ 3,600) and 209 nm (ϵ 10,600); MS *m/e* 208 (M^+); NMR ($CDCl_3$): H-2 (δ 6·99 ppm; J = 2·0; 1·5 Hz); H-5 (δ 6·93 ppm; J = 9·0; 1·0 Hz); H-6 (δ 4·99 ppm; J = 9·0; 2·0; 1·5 Hz); H-1 (δ 1·72 ppm; unresolved multiplet); H-7 (δ 1·72 ppm; unresolved multiplet); 2 Me-8 centered at δ 1·32 and 0·88 ppm. (Found: C, 63·3; H, 8·0; N, 13·2. Calcd. for $C_{11}H_{16}N_2O_2$: C, 63·44; H, 7·74; N, 13·45%).

4 - Ethoxycarbonyl - 5 - parabromobenzoyl - 8,8 - dimethyl - 3,4,9,10 - tetraza - tricyclo[5.3.0.0^{1,4}]deca - 2,9 - diene **23**. To a stirred soln of **22** (300 mg; 1·2 mmole) in 5 ml anhyd ether at 0° under argon atmosphere, 100 mg sodium hydride was added. After 1 h gas evolution ceased and freshly prepared p-bromobenzoyl chloride (300 mg; 1·37 mmole) was added. The mixture was stirred for another 4 h at room temp and 30 ml chloroform was added. The organic soln was washed successively with water, Na_2CO_3 aq, HCl aq, with water again and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was chromatographed over silicic acid thick layer plates with ethyl acetate/cyclohexane 5/5. Benzoate **23** was obtained as colourless crystals from acetone/hexane 1/1 (83 mg; 16%) which were suitable for X-ray analysis, m.p. 132–133°; IR (KBr) ν (C—H) 3060 cm^{-1} (cyclopropyl hydrogens), ν (C═O) 1760 and 1730 cm^{-1}, ν (C═N) 1630 cm^{-1}, ν (C═C) 1600 cm^{-1} and ν (N═N) 1530 cm^{-1}; UV ($CHCl_3$) λ_{max} 326 nm (ϵ 420) and 257 nm (ϵ 6,500); MS *m/e* 434,436 (M^+); (Found: C, 48·9; H, 4·2; N, 12·9; Br, 20·8. Calcd. for $C_{18}H_{15}N_4O_4Br$: C, 49·70; H, 4·17; N, 12·88; Br, 18·37%).

4 - Ethoxycarbonyl - 8,8 - dimethyl - 3,4,9,10 - tetraza - tricyclo[5.3.0.0^{1,4}]deca - 2,9 - diene - 5 - one **24**. To a soln of **22** (600 mg; 2·38 mmoles) in acetone (4 ml), at 2° under N_2, 2 ml of Jones' reagent[17] was added dropwise and the mixture stirred at room temp for 3 h. The filtrate was diluted with chloroform, treated twice with $NaHCO_3$ aq, then with brine and dried over Na_2SO_4. After evaporation of the solvents *in vacuo*, the remaining oil was chromatographed over silicic acid thick layer plates with ethyl acetate/cyclohexane 4/6. After a few days at 0° compound **24** crystallized (310 mg; 52% yield), m.p. 83–84° (pale yellow crystals); IR (KBr) ν (C—H) 3060 cm^{-1} (cyclopropyl hydrogens), ν (C═O) 1780 and 1730 cm^{-1}, ν (C═N) 1640 and ν (N═N) 1530 cm^{-1}; UV ($CHCl_3$) λ_{max} 330 nm (ϵ 350) and 243 nm (ϵ 7,100); MS *m/e* 250 (M^+). (Found: C, 52·9; H, 5·5; N, 22·3. Calcd. for $C_{11}H_{14}N_4O_3$: C, 52·79; H, 5·64; N, 22·39%).

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