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Seven-Membered Heterocyclic Rings

I. Formation of Substituted 4H-1,2-Diazepines from 2,4,6-Triarylpyrylium Salts and Hydrazine *

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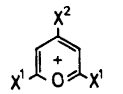
The formation of 3,5,7-triaryl-4H-1,2-diazepines from the reaction of 2,4,6-triarylpyrylium salts with hydrazine is reported. The structure assigned to the products is mainly based on proton magnetic resonance data and mass spectrometry. The electron impact induced degradation is discussed. From the nuclear magnetic resonance spectroscopic data it is concluded that the energy barrier for inversion between the two degenerate boat conformations of the diazepines (II′ ⇌ II″) is exceptionally large. For 3,5,7-triphenyl-4H-1,2-diazepine (IIa) the free energy of activation ($\Delta G^{\ddagger}$) was determined in a series of solvents. No evidence for a valence-tautomerization (II ⇌ III) was found.

Previously [1] it was reported that 2,4,6-triphenylpyrylium perchlorate (Ia, ClO_4^-) reacted with hydrazine to give a compound which was tentatively assigned the diazepine structure (IIa).** In this paper we substantiate the

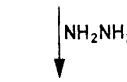
* This reaction was independently found in the laboratories in Bucharest [1] and Copenhagen. After realizing this it was decided to publish one joint full paper instead of two separate ones.

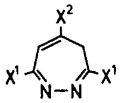
** Klingsberg [2] reported that 2,4,6-triphenylthiapyrylium salts reacted with hydrazine to give a compound which was assigned the structure IIa. However, no details were published. This led us to prepare 2,4,6-triphenylthiapyrylium tetrafluoroborate which was reacted with hydrazine and the product was found to be identical with IIa (IR and NMR spectroscopy, and mixed m.p. test).

tentative structure assignment [1] for IIa and show that this reaction, which we consider of obvious preparative interest, is of general character for 2,4,6-triarylpyrylium salts.

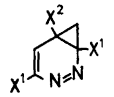


I, A^-





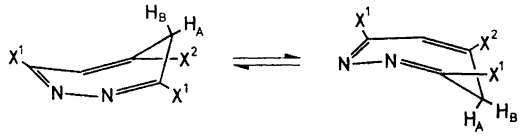
II



III

	X^1	X^2
a	C_6H_5	C_6H_5
b	»	p-$CH_3-C_6H_4$
c	»	p-$CH_3O-C_6H_4$
d	»	p-$Cl-C_6H_4$
e	»	p-$Br-C_6H_4$
f	»	p-$NO_2-C_6H_4$
g	»	m-$NO_2-C_6H_4$
h	p-$CH_3-C_6H_4$	p-$CH_3O-C_6H_4$
i	»	m-$NO_2-C_6H_4$
j	p-$Br-C_6H_4$	C_6H_5
k	»	p-$NO_2-C_6H_4$

A further impetus for this work was the possibility to determine whether compounds II were in tautomeric equilibrium with their valence isomers III. No positive evidence for the presence of such an equilibrium was found by an NMR analysis of compounds IIa–k. The NMR analysis, however, showed that the free energy of activation ($\Delta G^{\ddagger}$) for interconversion between the two nonplanar forms II'a and II''a is surprisingly large (Table 4).



II' II''

RESULTS

All of the 2,4,6-triarylpyrylium salts (I, $A^- = BF_4^-$) reacted with hydrazine to give almost quantitative yields of 4H-1,2-diazepines (II) (Table 1). The assignment of structure II to these compounds is based on their elemental analysis, and their nuclear magnetic resonance and mass spectra. The UV and IR spectra of compounds II do not allow any definite conclusions to be drawn with regard to their structure, but they are in agreement with our assignment (Table 2).

Table 1. 3,5,7-Triaryl-4H-1,2-diazepines.[a]

	M.p.	% C		% H		% N		% Halogen	
Compound	°C	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
IIa[b]	191–92[1]	85.30	85.68	5.70	5.63	8.60	8.69		
IIb	189–90	85.80	85.68	6.10	5.99	8.41	8.33		
IIc	153–54	81.68	81.79	5.92	5.72	8.01	7.95		
IId	188–89	77.10	77.39	4.83	4.80	7.80	7.85	Cl 10.06	9.93
IIe	181–82	68.80	68.84	4.38	4.27	7.07	6.98	Br 19.90	19.91
IIf	231–32[d]	75.34	75.19	4.73	4.66	11.29	11.44		
IIg	198–99[d]	74.95	75.19	4.79	4.66	11.33	11.44		
IIh	170–71	81.90	82.07	6.48	6.36	7.62	7.36		
IIi	227–28[d]	75.75	75.93	5.48	5.35	10.60	10.63		
IIj	256–57[d]	56.90	57.52	3.42	3.36	5.79	5.84	Br 33.66	33.29
IIk	254–55[d]	52.60	52.60	2.99	2.88	8.20	8.00	Br 30.41	30.43

[a] All the compounds (IIa–k) were obtained in almost quantitative yields.
[b] This compound [2] could be obtained in 90 % from 2,4,6-triphenylthiapyrylium tetrafluoroborate (superimposable IR spectra, same m.p., mixed m.p. test).
[d] Melts with decomposition. Melting points were taken in sealed capillaries.

Table 2. Characteristic ultraviolet and infrared absorptions of 4H-1,2-diazepines.

Compound	IR (in KBr) cm^{-1}	UV (in 96 % EtOH)					
		λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε
IIa	1604	209	4.47	258	4.50	293	4.35
IIb	1599	216	4.32	264	4.42	295	4.34
IIc	1608	209	4.56	270	4.50	293sh	4.46
IId	1599	209	4.48	261	4.52	292	4.38
IIe	1597	225	4.39	263	4.59	294	4.48
IIf	1594	213	4.34	245	4.22	285	4.35
IIg	1603	211	4.48	256	4.60	291sh	4.32
IIh	1603	209	4.54	271	4.46	302	4.44
IIi	1609	220	4.43	264	4.60	305sh	4.32
IIj	1598	215	4.14	267	4.30	300	4.20
IIk	1591	206	4.59	—	—	283	4.61

More substantial evidence was obtained from the NMR spectra of compounds II (Tables 3, 4). In each case where the solubility of the compound allowed cooling to a sufficiently low temperature we observed an eleven line ABX pattern which must be due to the non aromatic protons. By elevating the temperature, this part of the spectrum changes, first to a singlet at low field and an exchange broadened AB doublet at high field in the ratio 1:2 and by further elevation of the temperature, to two singlets in the ratio 1:2. The ABX pattern was verified by solvent change, decoupling experiments and

Table 3. Nuclear magnetic resonance spectra.[a]

Compound	Vinyl protons(X)[b]	Methylene protons[b,c] Exo (A)	Endo (B)	Aromatic protons	Other protons
IIa	3.32 t, 1H	5.58 d,d, J_{AX}=2.4, 1H,	J_{AB}=12.5, 7.37 d,d, J_{BX}=1.6, 1H	2.83–1.83, 15H	–
IIb	3.32 t, 1H	5.57 d,d, J_{AX}=2.3, 1H,	J_{AB}=11.9, 7.38 d,d, J_{BX}=1.5, 1H	2.83–1.83, 14H	$-CH_3$: 7.58s, 3H
IIc	3.36 t, 1H	5.58 d,d, J_{AX}=2.4, 1H,	J_{AB}=11.9, 7.41 d,d, J_{BX}=1.5, 1H	3.08–1.83, 14H	$-OCH_3$: 6.13s, 3H
IId	3.32 t, 1H	5.62 d,d, J_{AX}=2.4, 1H,	J_{AB}=12.0, 7.36 d,d, J_{BX}=1.5, 1H	2.75–1.83, 14H	–
IIe	3.32 t, 1H	5.63 d,d, J_{AX}=2.4, 1H,	J_{AB}=11.9, 7.35 d,d, J_{BX}=1.4, 1H	2.75–1.92, 14H	–
IIf[d]	3.23 s, 1H	5.63 d, 1H,	J_{AB}=12.0, 7.28 d, 1H	2.75–1.58, 14H	–
IIg	3.18 t, 1H	5.55 d,d, J_{AX}=2.3, 1H,	J_{AB}=12.2, 7.26 d,d, J_{BX}=1.5, 1H	2.75–1.42, 14H	–
IIh	3.40 t, 1H	5.62 d,d, J_{AX}=2.3, 1H,	J_{AB}=11.8, 7.45 d,d, J_{BX}=1.2, 1H	3.08–1.92, 12H	$-OCH_3$: 6.16s, 1H $-CH_3$: 7.70s, 1H, 7.60s, 1H
IIi[d]	3.26 s, 1H	5.65 d, 1H,	J_{AB}=12.5, 7.32 d, 1H	3.00–1.50, 12H	$-CH_3$: 7.68s, 1H, 7.60s, 1H
IIj[d]	3.36 s, 1H	5.65 d, 1H,	J_{AB}=12.0, 7.39 d, 1H	2.75–2.00, 12H	–
IIk[d]	3.27 s, 1H	5.67 d, 1H,	J_{AB}=12.5, 7.30 d, 1H	2.50–1.50, 12H	–

[a] The spectra were recorded in $CDCl_3$ with TMS as internal reference at 60 MHz with field sweep. The probe temperature was 0° for compounds IIa–e and IIg–h and 40° for compounds IIf and IIi–k. Chemical shifts are in τ-values, coupling constants in Hz. The analysis of the spectra were performed using the first order AMX approach. s=singlet, d,d=doublet of doublets, due to coupling with two nuclei with different coupling constants, t=distorted triplet, due to coupling with two nuclei with slightly different coupling constants.

[b] The pattern lost its fine structure upon heating. The AB pattern is converted to a single line upon further heating in higher boiling solvents.

[c] Inspection of molecular models shows that the endo H(4) is placed in the shielding area of the N(1)–C(7) double bond and the AB signals at highest field are therefore assigned to the endo proton.

[d] The solubility of the compound in $CDCl_3$ did not allow cooling. The ABX pattern is broadened by unresolved long range coupling.

Table 4. Temperature dependency of the nuclear magnetic resonance spectrum of 3,5,7-triphenyl-4H-1,2-diazepine (IIa) in a series of solvents and the free energy of activation for the process IIa′ ⇌ IIa″.[a]

Solvent	$\Delta\nu_{AB}$[b]	J_{AB}[c]	T_c (°C)	$\Delta G_c^{\neq}$[d]
Bromobenzene	107.0±0.5	12.0±0.2	93±5	17.5±0.3
Pyridine-d_5	124.0±0.5	12.0±0.2	92±5	17.4±0.3
Deuteriobromoform	105.0±0.5	12.0±0.2	84±5	17.1±0.3
Trifluoroacetic acid	~120[e]	—	−12±5	~12[e]

[a] The spectra were recorded with field sweep at 60 MHz with TMS as internal standard and the r.f. field kept well below saturation. Several spectra were recorded in each solvent at each temperature with different sweep widths (10 Hz/cm and 2 Hz/cm). The temperature was determined by measuring the chemical shift difference between the signals from the CH_2 and OH protons of an ethylene glycol sample. E_a, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G_c^{\neq}$ for some of the diazepines will be determined by complete line shape analysis and the results will be published separately.

[b] The chemical shift difference between the non-equivalent methylene protons without exchange in Hz at 10°.

[c] The coupling constant without exchange in Hz at 10°.

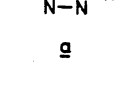
[d] The free energy of activation at the coalescence temperature (T_c) in kcal/mol is calculated using the formula $k_c=\pi(\Delta\nu_{AB}^2+6\,J_{AB}^2)^{\frac{1}{2}}/\sqrt{2}$ [14] and the Eyring equation assuming the transmission coefficient to be unity.

[e] Estimated values. The AB pattern is not resolved at the melting point of the trifluoroacetic acid solution. k_c is calculated from $1/2\tau=\pi\cdot\Delta\nu_{AB}/\sqrt{2}$.[15]

by recording the spectrum of IIa at 100 MHz. *A priori* a multitude of structures corresponding to the required elemental composition could be envisaged which could accommodate an arrangement of protons giving rise to an ABX pattern in the NMR spectrum. However, only structure II will accommodate the observed chemical shifts and coupling constants (Table 3) as well as the temperature dependence of the spectrum, which must be due to temperature dependent ring inversion (II′ ⇌ II″). The temperature dependence of the NMR spectrum of IIa in a variety of solvents has been examined and the energy of activation ($\Delta G^{\neq}$) calculated (Table 4).

The mass spectra of compounds II (Table 5, Figs. 1—4) also substantiate the structural assignment (II) to the products of reaction of hydrazine with 2,4,6-triarylpyrylium salts.

The mass spectra of the 4H-1,2-diazepines investigated can be rationalized using, IIa, IIc, IId, and IIe (Figs. 1, 2, 3, and 4) as typical examples. As seen from Figs. 1, 2, 3, and 4 the diazepines yield strong molecular ion peaks which are accompanied by less abundant M−1 species. Mechanistically the most probable source of hydrogen available for this fragmentation would be C-4, due to its allylic nature, such that the M−1 species can be represented as *a*.



a

Table 5. Partial mass spectra of 4H-1,2-diazepines (IIb and IIf–k).[a]

Compound	M^+	M−1	M−15	M−28	M−X^1CN	*e*	*e*−H·	*m/e* 115	*m/e* 103	Other significant processes
IIb	61	19	2	4	100	7	8	16	8	$[M-X^1CN]^{+}\cdot \xrightarrow[*]{-H\cdot}$ *m/e* 232 (16 %)
IIf	90	15	2	7	100	33	49	17	22	$[M-X^1CN]^{+}\cdot \xrightarrow[*]{-NO}$ *m/e* 234 (13 %)
IIg	85	10	–	7	100	25	38	17	14	$[M-X^1CN]^{+}\cdot \xrightarrow[*]{-NO}$ *m/e* 234 (14 %)
IIh	51	16	7	7	100	2	2	6	6	$[M-X^1CN]^{+}\cdot \xrightarrow[*]{-CH_3\cdot}$ *m/e* 248 (46 %)
IIi	83	11	1	12	100	18	14	13	2	
IIj	37	6	4	4	100	19	32	39	4	
IIk	32	7	2	12	100	22	10	28	10	$e \xrightarrow[*]{-Br}$ *m/e* 217 (50 %) $\xrightarrow[*]{-H\cdot}$ *m/e* 216 (39 %)

[a] The complete mass spectra of IIa and IIc–e are reproduced in Figs. 1–4. Ion intensities are expressed as percent of base peak and have been corrected for ^{13}C isotope contributions.

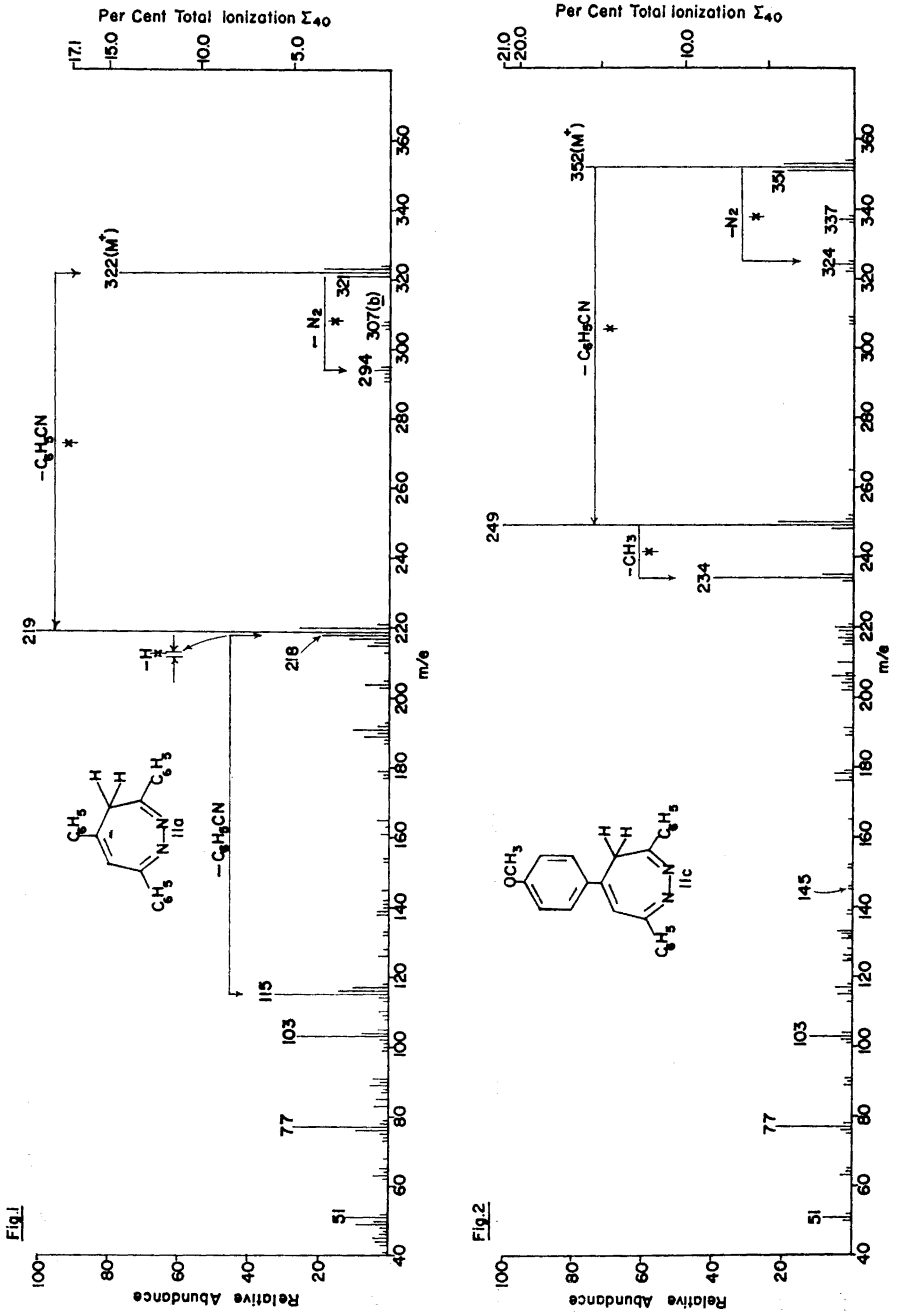


Fig. 1. Mass spectrum of 3,5,7-triphenyl-4H-1,2-diazepine (IIa).
Fig. 2. Mass spectrum of 5-(*p*-methoxyphenyl)-3,7-diphenyl-4H-1,2-diazepine (IIc).

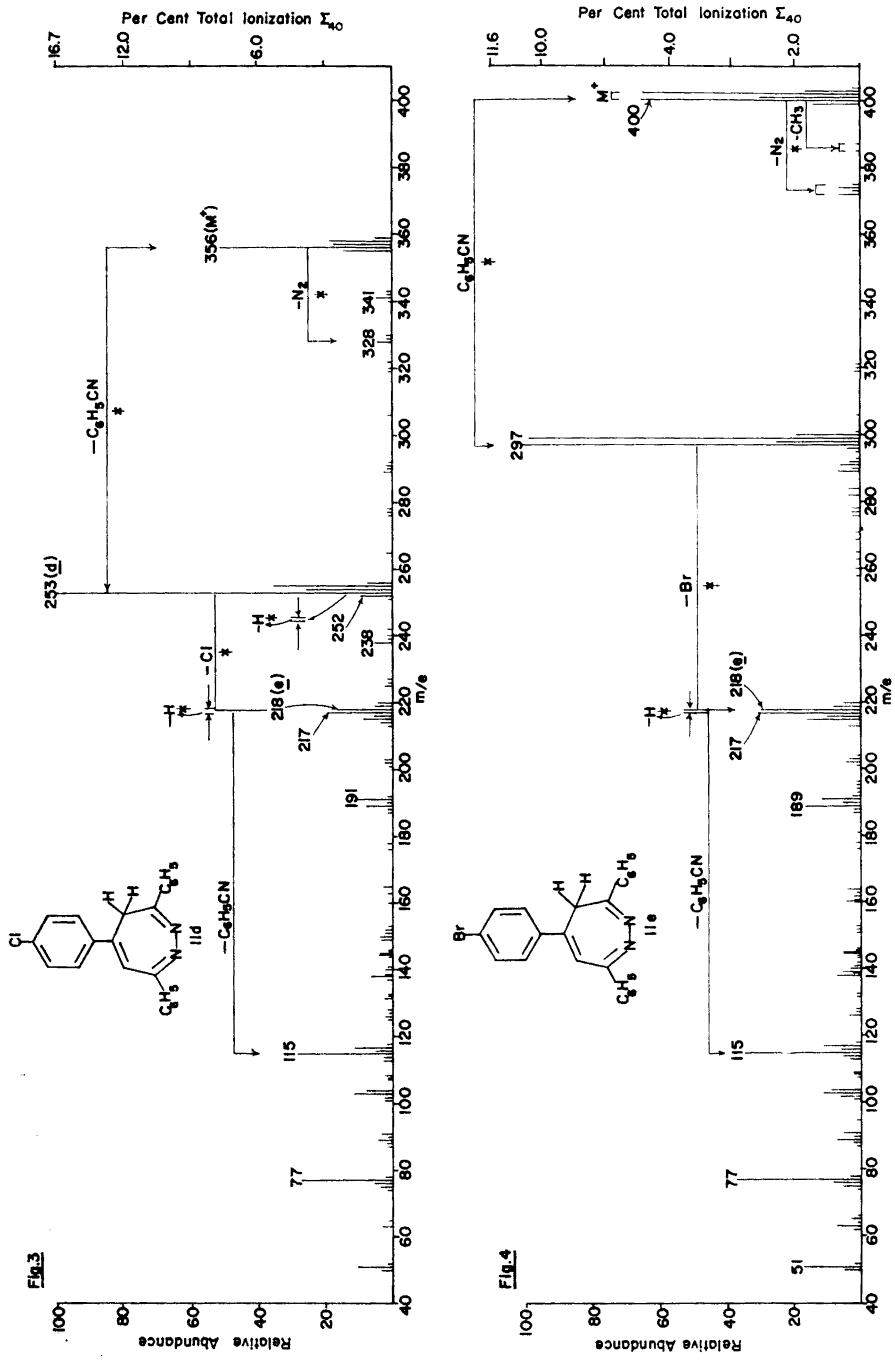
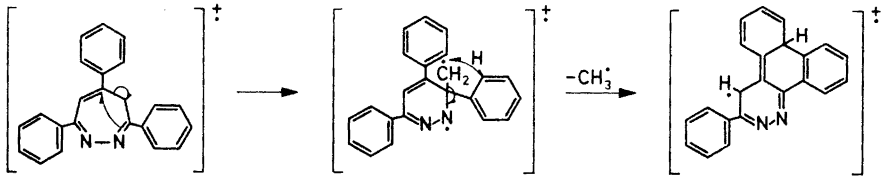


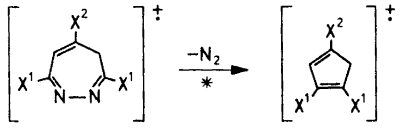
Fig. 3. Mass spectrum of 5-(*p*-chlorophenyl)-3,7-diphenyl-4H-1,2-diazepine (IId).
Fig. 4. Mass spectrum of 5-(*p*-bromophenyl)-3,7-diphenyl-4H-1,2-diazepine (IIe).

A low abundance, but mechanistically intriguing, peak occurs in the mass spectra of all the 4H-1,2-diazepines run and is due to the expulsion of a methyl group from their respective molecular ions. Using IIa as an example this can be rationalized in terms of *b*.



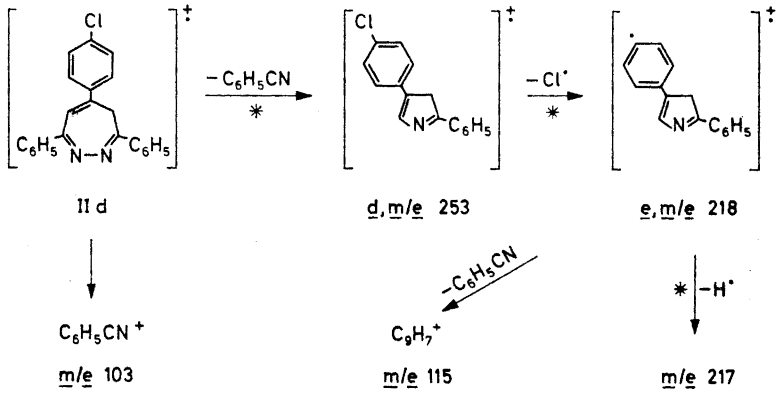
II a b, m/e 307

A ubiquitous fragmentation mode of the 4H-1,2-diazepines is the expulsion from their molecular ions of 28 amu. This process has analogy in the elimination of N_2 from heterocyclic structures containing two contiguous nitrogen atoms such as substituted pyridazines,[3,4] phthalazines,[3] tetrazines,[5] benzo[c]-cinnolines,[6] 1,2,4-triazines,[7] and 1,3,4-oxadiazoles,[8] respectively. In the case of the diazepines this formally corresponds to formation of the 1,2,4-trisubstituted cyclopentadiene ion radical *c*.



c

By far the major ion current in the fragmentation (often accompanied by the presence of a metastable ion) of the 4H-1,2-diazepines occurs by the expulsion of $X^1—C\equiv N$ and the resulting ion formally corresponds to *d* in



the case of IId. At low ionizing voltages (15 eV) this is the only fragmentation process to surpass 10 % relative abundance in those compounds investigated. In the analogues where X^1 is C_6H_5 the ion *d* is accompanied by a low intensity fragment at mass 103 which formally corresponds to ionized benzonitrile.

The 4H-1,2-diazepines (IId, IIe and IIj) in which X^1 or X^2 is substituted by a chlorine or bromine atom in the 4-position, suffer further fragmentation of the species *d* by the ejection of a halogen radical. This decomposition is of negligible intensity at low ionizing energy (15 eV), and the resulting species formally corresponds to *e* which in turn fragments by the ejection of a hydrogen atom. Those analogues investigated which lack halogen substitution in the 4-position of X^2 fragment to a species we depict as *e* by the loss of a hydrogen atom from *d*. It is noteworthy that IIc (Fig. 2), in which X^2 is substituted by a *para* methoxyl entity, yields an ion analogous to *d*. This fragment then expels a methyl radical which almost certainly arises from the methoxyl function.

A fragmentation, common to all the analogues studied except those bearing a *para* methoxyl group in X^2 is the loss of $X^1-C\equiv N$ from *e* with the formation of a conspicuous peak at mass 115 (see Figs. 1, 3, and 4). This ion virtually disappears at low ionizing voltages (15 eV) suggesting that it arises from a secondary decomposition process although no metastable ion could be discerned showing that it arose from *e*. The corresponding ion (*m/e* 145) attains only 1 % relative abundance in the mass spectrum (Fig. 2) of the methoxyl derivative IIc.

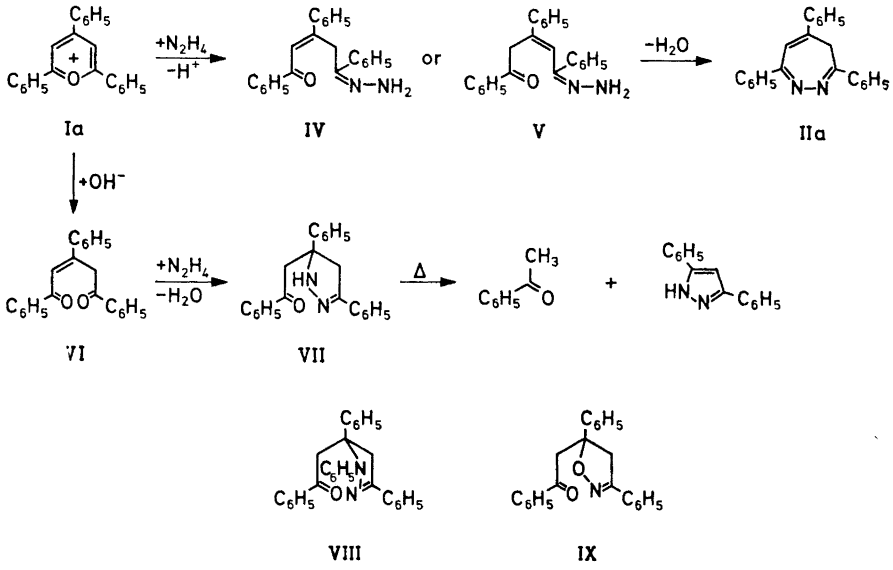
The reaction mechanism for the formation of the 1,2-diazepines is presently under investigation. However, some preliminary results have been obtained.*

If the reaction between Ia and hydrazine is carried out at room temperature in a two phase system (ether-water), the ethereal layer affords a colourless intermediate, m.p. 109°. This compound dehydrates extremely easily, thereby forming IIa. On the basis of its infrared spectrum (in CCl_4 and nujol) (which shows absorption at 1690 cm^{-1} (CO), 3290 cm^{-1} and 3395 cm^{-1} (NH)) and its nuclear magnetic resonance spectrum recorded in deuteriochloroform with TMS as internal standard (singlet at 3.40 τ (vinylic protons), singlet at 5.90 τ (methylene protons) and a broad signal centered at 4.12 τ ($-NH_2$) in the ratio 1:2:2) this intermediate is believed to have structure IV (resulting from an intramolecular 1,5-hydrogen transfer) or, less probably, structure V.

On the other hand, 1,3,5-triphenyl-2-pentene-1,5-dione (VI) (pseudobase of Ia) reacts differently with hydrazine. Behaving as an α,β-unsaturated ketone, it affords 5-phenacyl-3,5-diphenyl-2-pyrazoline (VII), m.p. 133°. Infrared data (in KBr): C=O absorption at 1675 cm^{-1}, NH absorption at 3400 cm^{-1}. Ultraviolet absorption maxima: 246 mμ (ε 15 000), 290 mμ (ε 11 500), and shoulders at 347 mμ (ε 2000) and 370 mμ (ε 1000) in 1,2-dichloroethane or ethanol. On heating above its m.p., or on treatment with acids, compound VII undergoes an elimination to give acetophenone and 3,5-diphenylpyrazole, identified by comparison with authentic specimens. The NMR spectrum of compound VII, recorded in deuteriochloroform with TMS as internal standard, presents, in addition to the AB quadruplet due to the ring methylene protons (6.10 τ and 6.48 τ, $J=17$ Hz), another AB quadruplet due to the phenacyl meth-

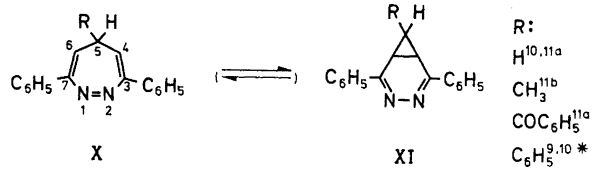
* These results will be communicated separately in more detail by A.T.B.

ylene protons (6.63 τ and 6.73 τ, $J = 16.4$ Hz). Magnetic non-equivalence of phenacyl protons can also be observed in the spectrum of 5-phenacyl-1,3,5-triphenyl-2-pyrazoline (VIII) [1] which also exhibits two AB quadruplets: ring methylene protons, 5.82 τ and 6.43 τ, $J = 18$ Hz; phenacyl methylene protons, 5.90 τ and 6.05 τ, $J = 17.2$ Hz. The phenacyl protons of 5-phenacyl-3,5-diphenyl-2-isoxazoline (IX) appear magnetically equivalent at room temperature.[1]



DISCUSSION

On the basis of our NMR spectroscopic examination of compounds II (Tables 3, 4) there is no evidence to suggest any valence-tautomerization between II and the, as yet, unknown III. Contrary to this, compounds of type XI have been isolated in several cases,[9–11] and it was inferred [10,11] that they exist in tautomeric equilibrium with their valence isomers (X). The former structure was found to be so preponderant that no direct evidence for structure X was observed. However, the facile *cis-trans*-isomerization of XI was presumed to occur with X as intermediate.[11] *



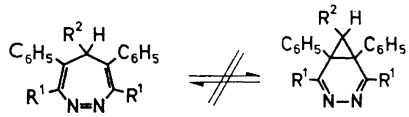
* It should be noted that it has been suggested [10] that X–XI (R=H) exist mainly as the latter at room temperature, but as X at 180°, on the basis of NMR spectroscopy. No details, however, were given.

It is interesting that a series of compounds of type XII has been found to exist preferentially in the diazepine form, apparently with no appreciable valence tautomerism to the bicyclic structure XIII.[10]

It was argued [10] that the preference for the bicyclic atomic arrangement for X—XI as apposed to the reverse situation for XII—XIII was due to the absence in case X—XI, *versus* the presence in case XII—XIII, of phenyl groups in the 4- and 6-positions. The extra conjugation provided by these phenyl groups in XII thus stabilizes it relatively to XIII.

We suggest that the preference for the monocyclic form in II—III as compared with the reverse situation in X—XI may be due, at least in part, to the difference in bonding at the nitrogen atoms.*

The $\Delta G^{\ddagger}$ for the ring inversion (IIa′⇌ IIa″, Table 4) is considerably larger than what has been found for other cycloheptatriene systems.[12] However, we will not attempt to rationalize this until further information has been obtained.



XII XIII

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of Chemical Laboratory II, University of Copenhagen, by Mr. Preben Hansen and his staff.

Melting points (uncorrected) were determined on a Büchi melting point apparatus in sealed capillaries.

Infrared spectra were recorded on a Perkin Elmer Model 337 grating infrared spectrophotometer.

Ultraviolet spectra were recorded on a Perkin Elmer Model 137 UV spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a Varian A 60 A spectrometer equipped with a Varian variable temperature controller (V 6040).

Mass spectra were obtained with an A. E. I. MS-9 instrument using direct sample insertion into the ion source (180°). The ionizing energy was maintained at 70 eV and low ionizing energy refers to nominal values only.

Pyrylium tetrafluoroborates (I, $A^- = BF_4^-$). These were all prepared according to the previously described method.[13] No elementary analyses were performed. The yields and melting points of the 2,4,6-triarylpyrylium salts (Ia and Ic—k, $A^- = BF_4^-$ and Ib, $A^- = FeCl_4^-$) are shown in Table 6. The tetrachloroferrate (Ib, $FeCl_4^-$) was prepared according to the method of Dilthey.[16]

3,5,7-Triaryl-4H-1,2-diazepines (II). These compounds were all prepared by adding *ca.* 2.5 mole of hydrazine hydrate to 1 mole of pyrylium salt suspended in ethanol (5 l/mole of pyrylium salt) with vigorous stirring at room temperature. In most cases a clear solution formed from which the diazepine crystallized after a few minutes. In some cases, however, when no clear solution was formed, the suspension was boiled for 10 min and left to cool at room temperature after which time all of the pyrylium salt had reacted. The diazepines were filtered off and recrystallized once or twice from ethanol to analytical purity. These results are summarized in Table 1.

* Generally species with N=N-bonding are found to be less stable than those with C=N-bonding.

Table 6. Yields and melting points of 2,4,6-triarylpyrylium salts (I, $A^- = BF_4^-$ or $FeCl_4^-$).

Compound	Ia, BF_4^-	Ib, $FeCl_4^-$	Ic, BF_4^-	Id, BF_4^-	Ie, BF_4^-	If, BF_4^-	Ig, BF_4^-	Ih, BF_4^-	Ii, BF_4^-	Ij, BF_4^-	Ik, BF_4^-
m.p. (°C)	228–30	224–27	239–42	264–68	—	297 d	256 d	300 d	290 d	308 d	303 d
Yield(%)	30	16	20	43	23	11	11	47	13	35	13

d = decomposition.

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