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ON THE CYCLISATION OF N-ALKYLFORMAZANS TO LEUCOVERDAZYLS (1,2,3,4-TETRAHYDRO-s-TETRAZINES)

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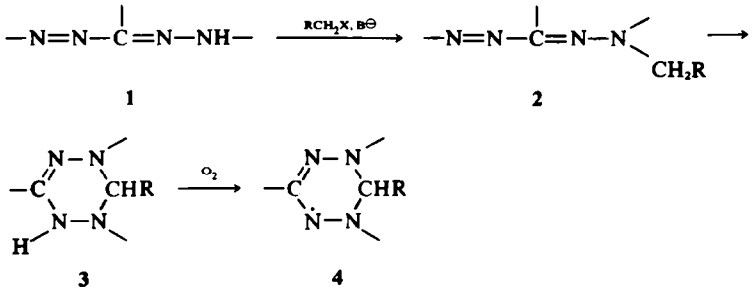
Abstract—A series of N-alkylformazans have been prepared and their cyclisation to leucoverdazyls studied. The cyclisation has been found to occur in the presence of strongly ionising bases, thermally, and in the presence of acid. The sensitivity of the cyclisation to the structure of the N-alkylformazans and to the cyclisation conditions are discussed in terms of mechanisms proposed for the reaction.

INTRODUCTION

Verdazyls **4**, which are cyclic hydrazidinyl radicals noteable for their extraordinary stability,[1] were discovered by Kuhn and Trischmann during attempts to alkylate formazans,[2] and this reaction is still the main route of preparing verdazyls. It has been experimentally verified[3] that alkylation first leads to the formation of N-alkylformazans **2**, which in solution cyclise, many even at room temperature, to give leucoverdazyls **3** (1,2,3,4-tetrahydro-s-tetrazines), which are then easily dehydrogenated by atmospheric oxygen to verdazyls **4**. In this sequence, the cyclisation of the N-alkylformazans **2** to leucoverdazyls, formally an addition of a primary alkyl function to an azo double bond, is an unusual reaction, and there is only a slight analogy with the addition of N,N-dimethylaniline to azodicarboxylic acid ester.[4]



1 **2**

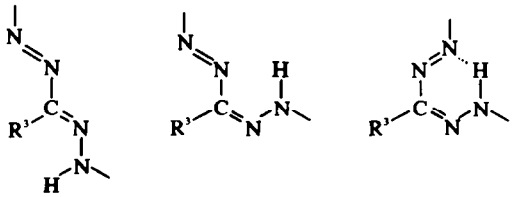
3 **4**

Preparation of verdazyls using the alkylation procedure leads, in a number of cases, to experimental difficulties, which would appear to come from the cyclisation step. Therefore, we have prepared a number of N-alkylformazans and studied closely the cyclisation **2**→**3** with a view to clarifying the mechanism of this controlling step in the syntheses of verdazyls by the alkylation procedure.

N-*Alkylformazans*

Treatment of the appropriate formazan **1** with a primary alkyl halide in DMF in the presence of base [BaO, $Ba(OH)_2 \cdot 8H_2O$] yielded the N-alkylformazans shown in Table 1. The choice of the alkylating agent in the alkylation of formazans seems to be restricted to primary alkyl compounds. For the present all attempts to synthesise N-alkylformazans with secondary or tertiary alkyl functions have been unsuccessful.

For N-alkylformazans two different forms are possible, namely *trans-anti* (**17**) and *trans-syn* (**18**) isomers. The existence of formazans (**1**) in two isomeric forms depending on the bulk of the substituent at the central C atom (C-3) is established.[1,8] When the substituent is small (H, Me) or orthogonal to the tetraazapentadiene system (2,6-dimethoxyphenyl[9]) the formazan occupies a linear, so-called, "yellow" *trans-anti* form **17**; when the substituent is larger (phenyl, t-Bu) the tetraazapentadiene system is sterically constrained to occupy a *trans-syn* form **18**, in which strong intramolecular H-bonding further stabilises the molecule in the *s-cis* conformation **19**.[10] Most of these "red" formazans can be converted for a short time to the yellow *trans-anti* isomers (**17**) by irradiation, the *trans-syn, s-cis* form **19** being regenerated on removal of the energy source.[7-9]



17: *trans-anti* **18**: *trans-syn* **19**: *trans-syn, s-cis*

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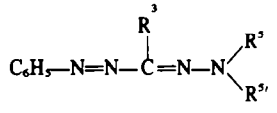
Table 1. N-Alkylformazans prepared



N-Alkyl-formazan	R^3	R^5	$R^{5'}$	m.p. (dec)
5	H	C_6H_5	CH_3	93–94°[3]
6	H	C_6H_5	CD_3	94–95°
7	H	C_6H_5	$CH_2C_6H_5$	134–135°
8	CH_3	C_6H_5	CH_3	77–78°[5]
9	C_6H_5	C_6H_5	CH_3	106–107°[3]
10	C_6H_5	C_6H_5	CD_3	106–107°
11	C_6H_5	C_6H_5	CH_2CH_3	90–94°
12	C_6H_5	C_6H_5	$CH_2C_6H_5$	90–93°
13	$C_6H_4OCH_3$-(4)	C_6H_5	CH_3	82–83°
14	C_6H_4Cl-(4)	C_6H_5	CH_3	87–89°
15	$C_6H_3(OCH_3)_2$-(2,6)	C_6H_5	CH_3	141–142°
16	C_6H_5	$CON(C_6H_5)_2$	CH_3	126–127°[6]

Similar arguments may, with some justification, be applied to N-alkylformazans, but, since they can no longer form hydrogen bonds, we cannot find direct spectroscopic evidence in this case. The quite different chemical behaviour of N-alkylformazans having small and large substituents at C-3, however, provides evidence for the existence of *trans-anti* and *trans-syn* isomers. N-Alkylformazans with a small substituent at C-3 (H: **5**, **6**, **7**; Me: **8**) are easily isolated and thermally stable in solution over a wide temperature range. Only on heating above 100°, and often at significantly higher temperatures, do these compounds cyclise in a nonuniform reaction to give, as the main product, leucoverdazyl. It seems that in this reaction an initial isomerisation of *trans-anti* to *trans-syn* isomers occurs followed by cyclisation.

The isolation of N-alkylformazans with a large substituent at C-3 (phenyl, t-Bu) is much more difficult; often spontaneous formation of leucoverdazyl at room temperature occurs, the half-life of N-methyl-triphenylformazan (**9**) in benzene at 40° being *ca* 1 hr. Attempts to isolate the N-alkyl-derivatives of 1,5 - bis(4 - methoxyphenyl) - 3 - phenylformazan, 1,5 - bis(4 - methylphenyl) - 3 - phenylformazan, 1,5 - bis(4-nitrophenyl) - 3 - phenylformazan and 3 - (4 - nitrophenyl) - 1,5 - diphenylformazan were unsuccessful due to the fast cyclisation; only the corresponding verdazyls or tetrahydro - s - tetrazines could be isolated. Additional chemical evidence for the existence of *trans-anti* and *trans-syn* N-alkylformazans in also provided by their reaction with acids (compare the corresponding section).

As **21** shows, in the possible *s-cis* conformation of the *trans-syn* isomer **20** the terminal azo nitrogen, the alkyl function and the alkylated nitrogen are in close spatial contact. Ability to attain this conformation seems to be the primary condition for the cyclisation.

A closer study of the cyclisation showed that it can occur under three distinctly different reaction conditions, namely in the presence of strong bases, thermally, and in the presence of acids.

The cyclisation in the presence of strong bases

Solutions of the N-alkylformazans in DMF or DMSO show, on addition of strong ionising bases such as sodium ethoxide or potassium t-butoxide, a deepening in colour which quickly fades in the case of the N-alkylformazans bearing large substituents at C-3, e.g. phenyl. The alkyl anion **22** produced cyclises to leucoverdazyl anion **23** which may either be protonated (**24**), oxidised (**25**), or, when formed in the alkylation procedure, further alkylated (**26**).

This reaction explains the isolation of tetrahydro-s-tetrazines (**26**) on alkylation of red formazans with electron acceptor substituents such as 4-nitrophenyl at N-1 and N-5 or at C-3 (Experimental), in that such substituents would increase the acidity of the α-hydrogens in the alkyl function. On neutralisation of solutions from N-alkylformazans with small substituents at C-3 (H or Me) and base, the N-alkylformazan may be recovered unchanged.

The thermal cyclisation

The thermal cyclisation of N-alkylformazans bearing a large substituent (phenyl, t-Bu) at C-3 in many organic solvents (Table 2) yields leucoverdazyls quantitatively in a reaction which follows first order kinetics (Fig 1). This reaction is not influenced by normal exposure to light, nor by radical initiators (e.g. t-butylpercinnamate) or inhibitors (e.g. *p*-phenylenediamine); when the cyclisation is followed by NMR, no CIDNP effect is observed. These results indicate that the thermal cyclisation is not a radical reaction. The rate of the cyclisation is only slightly altered by changing the solvent (Table 2) and shows no obvious dependence on solvent polarity. Replacement of the Me group in **9** by CD_3 (**10**) leaves the reaction rate almost

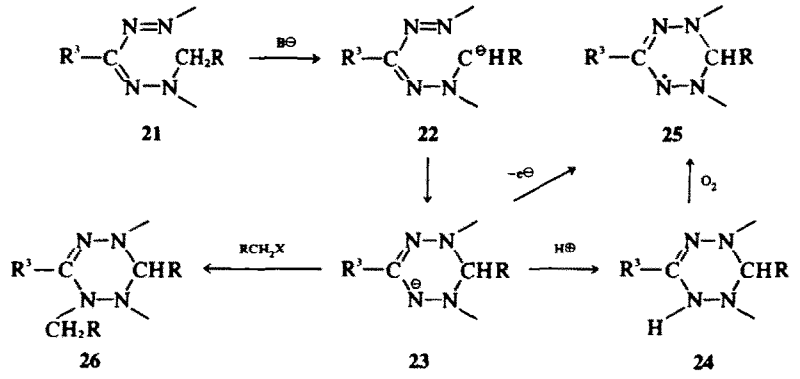
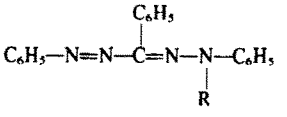


Table 2. First order rate constants ($s^{-1} \times 10^5$) for the cyclisation of **9** at 48·4°C, solvent dependence

Solvent	Rate constant
Ethanol	15·3
Dimethylformamide	18·2
Methanol	18·3
Pyridine	20·5
Dioxane	21·8
Benzene	23·2
Benzene (absence of light)	23·3
N,N-dimethylaniline	25·5
Diethylamine	27·0
Triethylamine	31·0

Table 3. First order rate constants ($s^{-1} \times 10$) for the cyclisation of N-alkylformazans at 48·4° in benzene



	R	Rate constant
9	CH_3	23·2
10	CD_3	22·5
11	CH_2CH_3	115
12	$CH_2C_6H_5$	77

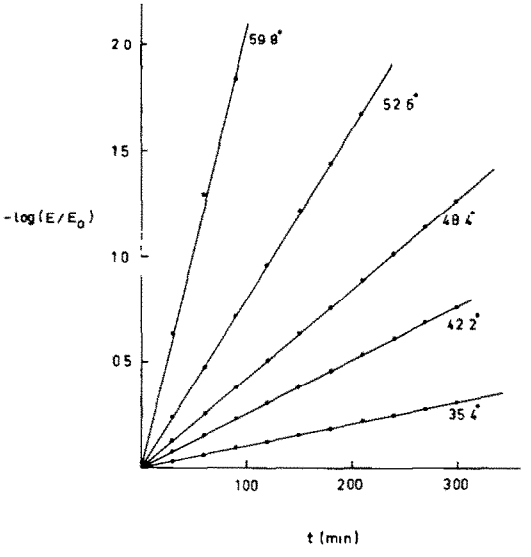
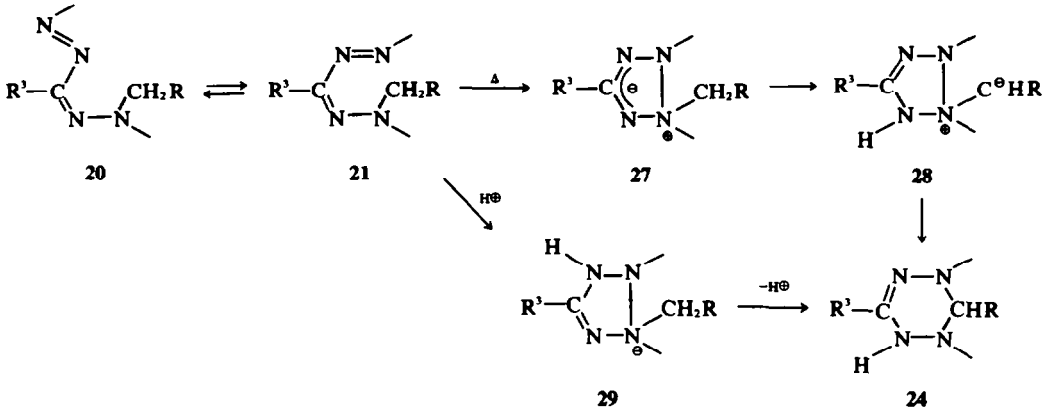


Fig. 1. Plot of $-\log(E/E_0)$ vs time for **9** in DMF (λ_{max} = 408 nm).

unchanged, no first order isotope effect is observed, while replacement of methyl by ethyl (**11**) or benzyl (**12**) increases the rate of the reaction only by a factor of five (Table 3). These kinetic results unambiguously show that the cleavage of the C–H bond in the N-alkylformazans does not occur in the rate determining step. Attempts to exchange the deuterium during the cyclisation of **10** in methanol gave no insertion of hydrogen either in the N-Me function of the N-alkylformazan nor in the methylene bridge of the leucoverdazyl, and vice versa during cyclisation of **9** in deuterated methanol.

From the results obtained it follows that the thermal cyclisation is a *multistep* reaction, for which we propose the mechanism shown below. The rate determining step is probably the formation of the delocalised zwitterion **27** which then undergoes a fast proton transfer to give the isomeric ylid **28**, followed by a Stevens-type rearrangement of the ylid to the leucoverdazyl (**24**). Proton shift and ring enlargement are fast processes, as we do not observe deuterium exchange in the methylene bridge. The observed nondependence of the rate on the solvent polarity does not contradict the assumption of the formation of a zwitterion in the rate determining step when one considers that the zwitterion **27** and the direct precursor **21**, the N-alkylformazan in the *s-cis* conformation, have about the same dipole moment.

p-Substituents in the 3-phenyl ring show some effect on the rate in agreement with the mechanism in that **13** ($R^3 = C_6H_4OCH_3$-(4), electron releasing) cyclises more slowly and **14** ($R = C_6H_4Cl$-(4), electron withdrawing) more quickly than **9** ($R^3 = C_6H_5$); the effect, however, is too small to be significant. Cyclisation of **15** is first order but slow due to the nonplanarity of the 2,6-dimethoxyphenyl group at C-3 with the formazan system (Fig 2).



20 21 27 28 29 24

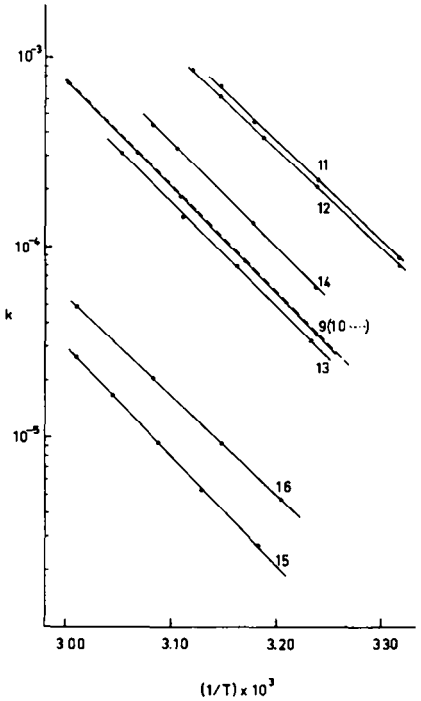


Fig. 2. Plot of log k vs (1/T) for the N-alkylformazans **9–16** in DMF.

Electron releasing *p*-substituents in the N-phenyl rings should accelerate the cyclisation. The failure of our attempts to prepare the N-alkyl derivatives of 1,5 - bis(4 - methylphenyl) - 3 - phenylformazan and 1,5 - bis(4 - methoxyphenyl) - 3 - phenylformazan may be ascribed to the fast thermal cyclisation of the N-alkylformazan intermediates and consequent formation of leucoverdazyls (verdazyls) in agreement with the mechanism proposed. The alkylation of nitro-substituted formazans yielded the corresponding 1 - methyl - 1,2,3,4 - tetrahydro s - tetrazines; due to the higher acidity of the N-methyl hydrogens the formed N-methylformazans cyclise immediately in the presence of base.

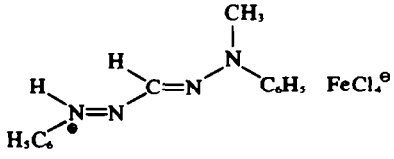
Table 4. Thermodynamic parameters for N-alkylformazan cyclisation in DMF (see Fig 2.)

N-Alkyl-formazan	$\Delta H^{\ddagger}$(kcal mole^{-1})	$\Delta S^{\ddagger}$(e.u.)	$\Delta G^{\ddagger}_{320°}$ (kcal mole^{-1})
9	+25·0	+2·1	+24·3
10	+25·0	+1·9	+24·4
11	+23·4	+0·6	+23·2
12	+23·5	+0·6	+23·3
13	+24·5	−0·1	+24·5
14	+24·6	+0·6	+24·3
15	+25·9	−1·7	+26·4
16	+23·3	−8·3	+25·9
9[a]	+25·0	+2·8	+24·2
13[a]	+22·6	−5·3	+24·3
14[a]	+24·0	+0·3	+23·9

[a] Values measured in benzene for comparison.

The cyclisation in the presence of acids

In the presence of acid N-alkylformazans bearing a small substituent at C-3 form stable tetraazapentadienium ions, which may be isolated as their $FeCl_4^{\ominus}$ salts (**30**). N-alkylformazans with large substituents (C_6H_5, t-Bu) at



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C-3, however, show quite different behaviour. On addition of traces of acid, e.g. acetic acid or hydrochloric acid, to a solution of these N-alkylformazans in DMF, the cyclisation is promoted in less than a second giving leucoverdazyl as the only major product. A possible explanation of the strong acid effect on the cyclisation may be that the formation of the protonated form of the delocalised zwitterion (**29**) is greatly facilitated by protonation of the azo double bond in the N-alkylformazans.

EXPERIMENTAL

UV spectra were obtained using a Cary 14 spectrophotometer, mass spectra using a Dupont 21–492 mass spectrometer. All m.ps. are uncorrected.

3,5 - Dimethyl - 1,5 - diphenylformazan,[5] 5 - methyl - 1,3,5 - triphenylformazan,[3] 5 - diphenylcarbamoyl - 5 - methyl - 1,5 - diphenyl - formazan[6] and t-butylpercinnamate[11] were prepared as described in the literature.

5-Methyl-1,5-diphenylformazan[3] (**5**). 1,5-Diphenylformazan[12] (3 g) in DMF (70 ml) + BaO (15 g) + $Ba(OH)_2 \cdot 8H_2O$ (1 g) were cooled to 0° and MeI (5 ml) added. After stirring at room temp for 24 hr, the mixture was partitioned between benzene and water, the benzene layer washed 5 times with water, dried ($MgSO_4$) and the solvent evaporated. The residue gave, on recrystallisation from MeOH, yellow plates (1·5 g), m.p. 93–94° (lit.[3] 93–94°).

5-Trideuteromethyl-1,5-diphenylformazan (**6**). 1,5-Diphenylformazan[12] (2·6 g) in DMF (70 ml) + BaO (15 g) + $Ba(OH)_2 \cdot 8H_2O$ (1 g) at 0° were treated with trideuteromethyl iodide (2 g) for 24 hr and worked up, as described above (**5**), to yield orange-red prisms (1·2 g), from MeOH, m.p. 94–95° (Found: C, 69·7; H + D, 7·1; N, 23·0. $C_{14}H_{11}D_3N_4$ requires: C, 69·7; H + D, 7·1; N, 23·2%).

5-Benzyl-1,5-diphenylformazan (**7**). 1,5-Diphenylformazan[12] (2·2 g) in DMF (30 ml) + BaO (5 g) + $Ba(OH)_2 \cdot 8H_2O$ (0·8 g) at room temp. were stirred with benzyl bromide (2 g) for 18 hr and worked up, as described above (**5**), to yield orange-red prisms (2·3 g), from MeOH, m.p. 134–135° (Found: C, 76·4; H, 5·7; N, 17·8. $C_{20}H_{18}N_4$ requires: C, 76·4; H, 5·8; N, 17·8%).

5-Trideuteromethyl-1,3,5,-triphenylformazan (**10**). 1,3,5-Triphenylformazan[12] (1·5 g) in DMF (40 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −10° were stirred with trideuteromethyl iodide (5 g) for 10 min, and quickly worked up, as described above (**5**), to yield orange-red prisms (300 mg), from benzene/hexane, m.p. 106–107° (dec) (Found: C, 75·4; H + D, 6·8, N, 17·7. $C_{20}H_{15}D_3N_4$ requires: C, 75·7; H + D, 6·7; N, 17·7%).

5-Ethyl-1,3,5,-triphenylformazan (**11**). 1,3,5-Triphenylformazan[12] (1·5 g) in DMF (40 ml) + BaO (5 g) + $Ba(OH)_2 \cdot 8H_2O$ (1 g) at −10° were stirred with EtI (10 g) for 20 min. and quickly worked up, as described above (**5**), to give a brown gum which was further purified by rapid chromatography (twice) on Al_2O_3 (Brockmann), using cyclohexane as eluent, to yield orange prisms (50 mg) form MeOH, m.p. 90–94° (dec) (Found: C, 77·0; H, 6·3; N, 16·7. $C_{21}H_{20}N_4$ requires: C, 76·8; H, 6·1; N, 17·0%).

5-Benzyl-1,3,5,-triphenylformazan (**12**). 1,3,5-Triphenylformazan[12] (1·5 g) in DMF (40 ml) + BaO (5 g) + $Ba(OH)_2 \cdot 8H_2O$ (0·5 g) at −15° were stirred with benzyl bromide (0·8 g) for 4 hr and quickly worked up, as described above (**11**), to yield orange prisms (40 mg) from aqueous MeOH, m.p. 90–93° (dec) (Found: C, 79·8; H, 5·4; N, 14·2. $C_{26}H_{22}N_4$ requires: C, 80·0; H, 5·7; N, 14·3%).

3 - (4 - *Methoxyphenyl*) - 5 - *methyl* - 1,5 - *diphenylformazan* (**13**). 3 - (4 - Methoxyphenyl) - 1,5 - diphenylformazan[12] (0·75 g) in DMF (40 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −10° were stirred with MeI (5 g) for 10 min and quickly worked up, as described above (**5**), to yield orange prisms (220 mg), from benzene/hexane, m.p. 82–83° (dec) (Found: C, 73·2; H, 6·1; N, 16·5. $C_{21}H_{20}N_4O$ requires: C, 73·2; H, 5·9; N, 16·3%).

3 - (4 - *Chlorphenyl*) - 5 - *methyl* - 1,5 - *diphenylformazan* (**14**). 3 - (4 - Chlorphenyl) - 1,5 - diphenylformazan[12] (1 g) in DMF (30 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −10° were stirred with MeI (5 g) for 5 min and quickly worked up, as described above (**5**), to yield orange prisms (450 mg), from aqueous EtOH, m.p. 87–89° (dec). (Found: C, 68·7; H, 5·1; N, 16·3. $C_{20}H_{17}ClN_4$ requires: C, 68·9; H, 4·9; N, 16·1%).

3 - (2,6 - *Dimethoxyphenyl*) - 5 - *methyl* - 1,5 - *diphenylformazan* (**15**). 3 - (2,6 - Dimethoxyphenyl) - 1,5 - diphenylformazan[9] (0·4 g) in DMF (25 ml) + $Ba(OH)_2 \cdot 8H_2O$ (2 g) at 0° were stirred with MeI (2 g) for 15 min and worked up, as described above (**5**), to yield orange prisms (320 mg), from MeOH, m.p. 141–142° (dec) (Found: C, 70·3; H, 6·1; N, 14·9. $C_{22}H_{22}N_4O_2$ requires: C, 70·6; H, 5·9; N, 15·0%).

1,5 - *Bis*(4 - *methoxyphenyl*) - 3 - *phenylverdazyl*.[13] 1,5 - Bis(4 - methoxyphenyl) - 3 - phenylformazan[12] (1 g) in DMF (40 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −20° were stirred with MeI (10 g) for 10 min and quickly worked up, as described above (**5**) at low temp., to yield the verdazyl as dark green prisms (500 mg), from acetone/MeOH, m.p. 143–144° (lit.[13] 143–144°).

1,5 - *Bis*(4 - *methylphenyl*) - 3 - *phenylverdazyl*. 1,5 - Bis(4 - methylphenyl) - 3 - phenylformazan[12] (1 g) in DMF (40 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −20° were stirred with MeI (10 g) for 5 min and quickly worked up, as described above (**5**), to yield the verdazyl as dark green prisms (620 mg), from MeOH, m.p. 128–129° (Found: C, 76·8; H, 6·2; N, 16·3. $C_{22}H_{24}N_4$ requires: C, 77·4; H, 6·2; N, 16·4%).

1 - *Methyl* - 2,4 - *bis*(4 - *nitrophenyl*) - 6 - *phenyl* - 1,2,3,4 - *tetrahydro* - *s* - *tetrazine*. 1,5 - Bis(4 - nitrophenyl) - 3 - phenylformazan[12] (1·5 g) in DMF (40 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −20° were treated with MeI (1 g) for 5 hr and worked up, as described above (**5**), to yield the tetrahydro-s-tetrazine as yellow prisms (1·4 g), from aqueous acetone, m.p. 203–204° (Found: C, 60·5; H, 4·6; N, 20·3%; M^+, 418. $C_{21}H_{18}N_6O_4$ requires: C, 60·3; H, 4·3; N, 20·1%; M^+, 418).

1 - *Methyl* - 6 - (4 - *nitrophenyl*) 2,4 - *diphenyl* - 1,2,3,4 - *tetrahydro* - *s* - *tetrazine*. 3 - (4 - Nitrophenyl) - 1,5 - diphenylformazan[12] (1·5 g) in DMF (40 ml) + $Ba(OH)_2 \cdot 8H_2O$ (5 g) at −20° were stirred with MeI (1 g) for 2 hr and worked up, as described above (**5**), to yield the tetrahydro-s-tetrazine as yellow prisms (320 mg), from aqueous acetone, m.p. 154–155° (Found: C, 67·5; H, 5·1; N, 18·5. $C_{21}H_{19}N_5O_2$ requires: C, 67·5; H, 5·1; N, 18·7%).

Behaviour of N-alkylformazans in the presence of strongly ionising bases. Compound **5** (150 mg) was dissolved in DMF (20 ml) at 25° under N_2 and a molar solution of NaOEt (1 ml) was added. After stirring the mixture for 15 min 2 N HCl (0·5 ml) and a little $CaCO_3$ were added, the organic extract in ether was washed 4 times with water, dried ($MgSO_4$) and the solvent evaporated to give from MeOH the starting **5** (110 mg).

5-Methyl-1,3,5-triphenylformazan[3] (50 mg) treated as above yielded from MeOH 1,3,5-triphenylverdazyl (30 mg), m.p. 142–143° (lit.[3] 142–143°).

Kinetic measurements. The absorbance of the N-alkylformazans at their absorption maxima around 400 nm were measured against time. A weighed amount of the N-alkylformazan was dissolved in the appropriate solvent at 10° and the solution flushed with oxygen free nitrogen for 10 min before measurements were made.

Effect of acid on N-alkylformazans and isolation of $FeCl_4$*-salts.* To a soln of 5-methyl-1,5-diphenylformazan (250 mg) in formic acid (20 ml) was added a soln of $FeCl_3 \cdot 6H_2O$ (1 g) in H_2O (0·5 ml). After standing for 5 hr, the ppt formed was filtered off and dried to give **30**, as violet crystals (300 mg), m.p. 105–106°. UV in HCOOH, λ_{max} (log ϵ): 500 (4·96), 356 (3·76), 263 (4·34) (Found: C, 38·7; H, 3·6; N, 12·8; Fe, 13·0; Cl, 32·4. $C_{14}H_{15}Cl_4FeN_4$ requires: C, 38·5; H, 3·5; N, 12·8; Fe, 12·8; Cl, 32·5%).

5-Methyl-1,3-5-triphenylformazan (50 mg) in formic acid (1 ml), $FeCl_3 \cdot 6H_2O$ (200 mg) were treated as above to yield 1,3,5,-triphenylverdazylium-$FeCl_4$ (30 mg), m.p. 162–163° (lit.[13] 162–163°).

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