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PMR AND DMR STUDIES OF 1,5-DIPHENYLVERDAZYLS[1]

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Abstract—Using PMR and DMR the hfs H and D coupling constants for a series of substituted 1,5-diphenylverdazyls have been measured and assigned. The C-6 methylene proton resonance has been studied as a function of temperature. The results indicate a ring inversion in verdazyls which is slow on the NMR time scale. Furthermore, the gain in resolution is discussed obtained with PMR in DBNO, and with DMR.

INTRODUCTION

THE paramagnetic shifts δ_p of PMR spectra of neutral organic free radicals[2] and radical ions[3] have been shown to provide information in addition to that obtained from ESR spectra. Firstly, the NMR spectrum renders directly the sign of the coupling constant; secondly, small coupling constants below the resolvability of ESR can frequently be measured. This second advantage makes NMR particularly useful for the study of radicals like the verdazyls where comparatively high spin densities on nitrogen result in a larger linewidth of the ESR as compared to hydrocarbon radicals. When measuring NMR of nuclei with larger coupling constants the NMR linewidth may be broadened beyond detection, but it can be reduced by using the liquid free radical[4] di-tert.-butylnitroxide (DBNO) as a solvent.

We have measured the paramagnetic shift δ_p of protons and deuterons in numerous substituted 1,5-diphenylverdazyls with the following aims:

(1) To measure directly the magnitude and sign of hfs coupling constants, especially of the C-6 methylene protons, the resonance of which could not be observed hitherto.

(2) To check experimentally the gain in resolution obtained with deuteron resonance and for protons when using DBNO as solvent; furthermore to compare the coupling constants obtained in DBNO and in diamagnetic solvents.

THEORY

The hfs-splitting visible in ESR spectra is averaged out when observing NMR because of the short spin-lattice relaxation time τ_1 and/or the exchange time τ_e of the electronic spins. Instead, a paramagnetic shift is observed, the magnitude of which is defined by

$$\delta_p(T) = \frac{\nu_p - \nu_d}{\nu_d} = \frac{a_I h \gamma_S}{4kT\gamma_I} \qquad (1)$$

which can be written

$$a_I = C_I(T) \cdot \delta_p \qquad (2)$$

The constants $C_I(T)$ for protons and deuterons at room temperature are

$$C_H(295°K) = 3{\cdot}73 \cdot 10^{-2}\ \text{MHz/ppm} = 1{\cdot}33 \cdot 10^{-2}\ \text{Gauss/ppm and}$$
$$C_D(295°K) = 5{\cdot}73 \cdot 10^{-3}\ \text{MHz/ppm} = 2{\cdot}05 \cdot 10^{-3}\ \text{Gauss/ppm}$$

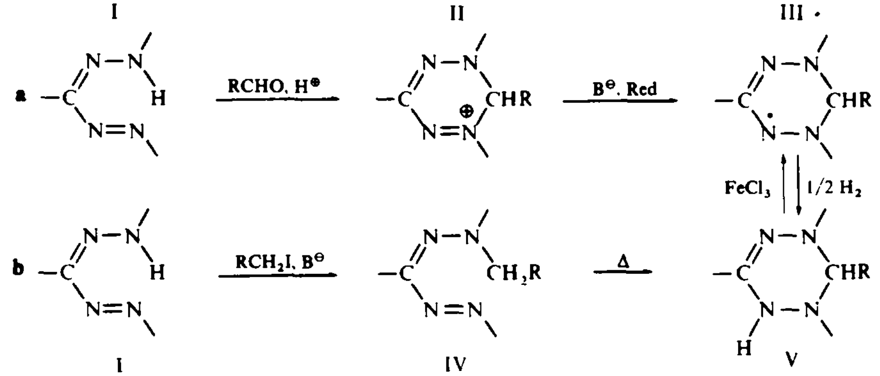
The paramagnetic shift of the deuterons as defined in (1) in ppm is, of course, identical with the shift of the protons, but the shift measured in Hz or Gauss is reduced by the factor $\gamma_P/\gamma_D \approx 6{\cdot}5$. However, since the linewidth $\Delta\nu$ is caused by the interaction between the nucleus concerned and the unpaired electron and is known to be proportional to the square of this interaction, one would expect a reduction of the linewidth of DMR by a factor of $\gamma_P^2/\gamma_D^2 \approx 6{\cdot}5^2 \approx 42$ with respect to protons and hence an increase in the resolution $\Delta\nu/\nu$ by a factor 6·5.

SYNTHESIS OF THE VERDAZYLS

The basic compounds in the synthesis of the verdazyls, the formazans I, were obtained by known procedures.[5] The verdazyls were prepared by two known reaction pathways,[6] with modifications of the procedures in some cases:

(a) By reaction of the formazan I with an aldehyde in the presence of an acid yielding the verdazylium cation II, and subsequent reduction to the verdazyl III under basic conditions (verdazyl VII, IX, XII, XIV, XV, XVI and XVIII).

(b) By methylation of the formazan I, thermal ring closure of the N-alkylformazan IV to give the leucoverdazyl V and subsequent oxidation to the verdazyl III with $FeCl_3$ under basic conditions (verdazyls VI, VII, VIII, IX, X, XI, XIII and XVII).



The diamagnetic leucoverdazyls V were used as reference compounds in the determination of the paramagnetic shifts. They were obtained by hydrogenation of the verdazyls III with 5% $Pd/BaSO_4$[7] as catalyst.

RESULTS AND DISCUSSION

The NMR spectra of all the verdazyls studied are resolved and exhibit resonance lines of all protons and deuterons except for those protons which are covered by the intense resonance band of the solvent DBNO often used. The resonance lines were assigned by comparison of the spectra and on the basis of ESR data obtained previously.[8] The measured paramagnetic shifts in ppm as well as in MHz and Gauss are listed in table 2. Representative spectra are shown in the Figs 1–3.

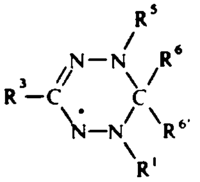


TABLE 1. VERDAZYLS PREPARED

Verdazyl	R^3	$R^1 = R^5$	R^6	$R^{6'}$	m.p. (dec)
VI	H	C_6H_5	H	H	109–110°[6]
VII	Me	C_6H_5	H	H	99–100°
VIII	Me	C_6H_5	D	D	101–102°
IX	CD_3	C_6H_5	H	H	97–98°
X	CD_3	C_6H_5	D	D	101–102°
XI	Me	C_6H_5	H	Me	109–110°
XII	CMe_3	C_6H_5	H	H	108–109°[1]
XIII	CMe_3	C_6H_5	D	D	110–111°
XIV	CMe_3	C_6D_5	H	H	106–107°
XV	CMe_3	C_6H_5	H	Me	82–83°
XVI	CMe_3	C_6H_5	D	CD_3	88–89°
XVII	COOEt	C_6H_5	H	H	127–128°[8]
XVIII	COOEt	$C_6H_3Cl_2$-(3, 5)	H	Me	121–122°

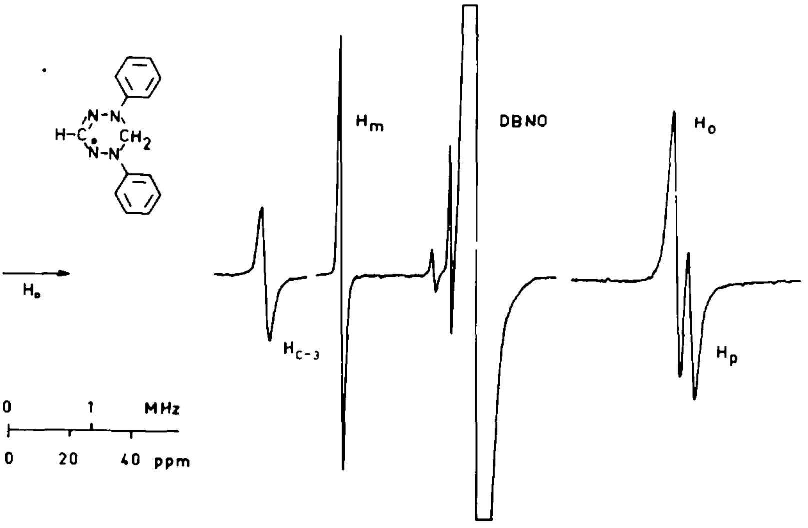


FIG 1. HMR spectrum of 1,5-diphenylverdazyl (VI) in DBNO

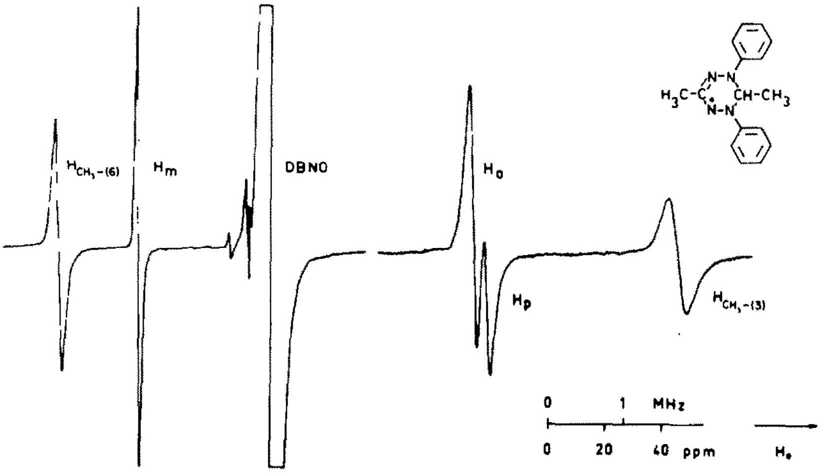


FIG 2. HMR spectrum of 3.6-dimethyl-1.5-diphenylverdazyl (XI) in DBNO

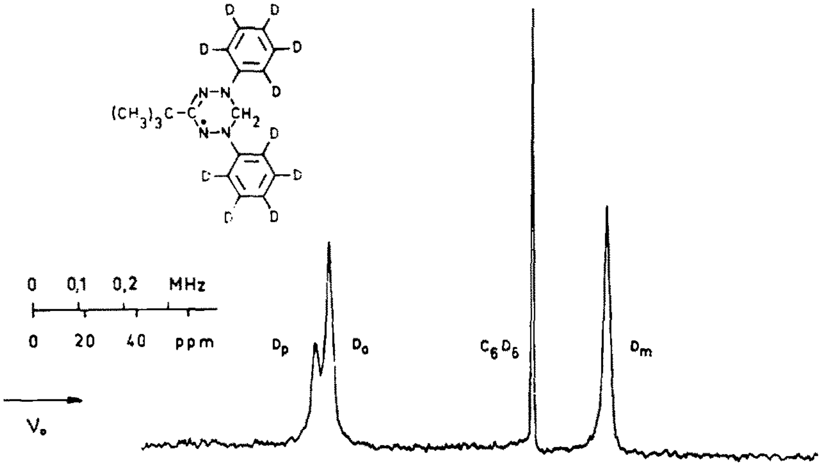
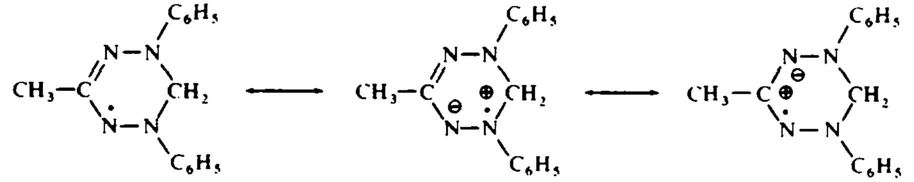


FIG.3. DMR spectrum of 3-t-butyl-1,5-di-pentadeuterophenylverdazyl (XIV) in DBNO

The coupling constants of the N-phenyl ring protons are almost constant in this series, confirming ESR results of verdazyls.[8] The NMR lines from the o- and p-protons (deuterons) in the N-phenyl rings are shifted to high field and yield a somewhat larger negative coupling constant for the p-protons than for the o-protons. The NMR line of the m-protons (deuterons) is shifted to low field and gives a positive coupling constant.

The proton coupling constants in R^3 are 0·72 Gauss for $>\mathrm{CH}$ (α, VI), $-2{\cdot}03$ Gauss for $>\mathrm{C{-}CH_3}$ (β, VII) and $+0{\cdot}11$ Gauss for $>\mathrm{C{-}CMe_3}$ (γ, XII). In this series the β coupling constant is unusually large and the γ coupling constant has the opposite sign respective to the sign of the spin density at C-3. The spin density at C-3 can be derived from the α coupling constant. The McConnell[9] equation $a_H = 23{\cdot}7\ \rho_{C-\alpha}$[10] yields $\rho_{C\text{-}3} = -0{\cdot}0304$, a value which agrees very well with McLachlan molecular orbital calculations.[11] Derived from ρ_{C-3} the β coupling constant for the freely rotating methyl group in VII should be about $-0{\cdot}9$ Gauss [$a_{CH_3} = 1/2\rho_{C-\alpha}\ (B_0 + B^H_{C-CH_3})$:[12] $B_0 < 4$.[13, 14] $B^H_{C-CH_3} = 56$–60 Gauss[15]] β coupling constants are accounted for mainly by hyperconjugation.[16] The extent of hyperconjugation depends strongly on a positive charge at the C atom substituted. In radical cations β coupling constants often are twice as large as in the parent radical anions.[17, 18] HMO calculations[11] yielded the following electron densities in the 1,5-diphenylverdazyl ring: N-1, N-5, 1·55; N-2, N-4, 1·48; C-3, 0·81. The nitrogens N-1 and N-5 have a net charge of +0·45, since they contribute two electrons to the π-system of the molecule; the C-3 contributing 1 electron has a net charge of +0·19. This charge distribution is represented by the resonance structures VIIa and b. The unusual high β coupling of the methyl protons in VII, twice as large as expected, can be explained by the presence of a considerable positive net charge at C-3 which amplifies the hyperconjugation. The γ coupling constant of the t-butyl protons can be interpreted by three types of interactions. If spin polarization is responsible the observed γ coupling constant should be positive as found, and proportional to the spin density atC-3, therefore very small (<0·05 Gauss[19]). A second mechanism, the transfer of spin density to the β-carbon via C—C hyperconjugation and then to the t-butyl protons via the usual spin polarisation, leads to the same sign and could account for the size of the measured γ coupling constant. A third mechanism, a direct polarization of the hydrogen's 1 s electron by the large positive spin densities at N-2 and N-4 in the verdazyl ring, would also result in a positive contribution to the coupling constant. Thus, each mechanism produces a positive sign, and one may be observing a combination of all three interactions.



VII VIIa VIIb

The NMR signals of the C-6 methylene protons were detected with some difficulty. Only DMR of the deuterated verdazyls VIII and XIII revealed clearly the location of the C-6 proton resonance. In DBNO this resonance is covered by the DBNO band, but in other solvents (CCl_4, C_6D_6) the C-6 proton signals can be detected. The C-6 methylene proton resonance is *one. remarkable broad* signal. which is slightly shifted to high field yielding a very small negative coupling constant. The magnitude of this shift follows eq. (1) when varying the temperature. Furthermore, the signal broadens even more at lower temperatures and sharpens at higher temperatures with respect to the other NMR signals of the verdazyl studied. On the other hand, the very small paramagnetic shift should give rise to a very narrow NMR signal. The opposed experimental findings (the equivalence of the two C-6 methylene protons within the linewidth and the remarkable temperature dependence of the broad signal) indicate a ring inversion of the type XIX ⇌ XX occurring in the verdazyl ring.

of XVIII (Fig 4). The coupling constant of the methyl protons is +2·37 MHz. This large coupling constant seems to be due to a direct polarization of the methyl hydrogen's 1 s electron by the large positive spin densities at N-1 and N-5 in the verdazyl ring. The signal of the remaining C-6 proton is again hard to detect. Knowing the resonance position from the DMR spectrum of XVI the respective resonance of the single C-6 proton can be found as a broad signal, shifted −4·4 ppm, in the NMR spectrum of XI dissolved in C_6D_6.

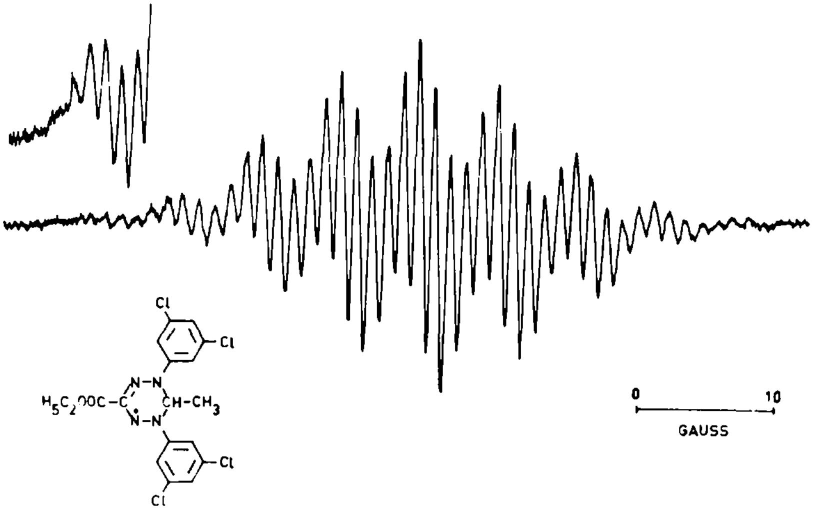


FIG 4. ESR spectrum of 6-methyl-3-ethoxycarbonyl-1,5-bis (3,5-dichlorophenyl)verdazyl (XVIII) in benzene; a^N = 5·75 Gauss (4 N); a^H = 1·15 Gauss (9 H, H_o, H_p, H_{CH_3})

We have studied the linewidths of the 3-CH_3, 6-CH_3, H_m, H_o, 3-CD_3, 6-CD_3, D_m and D_o resonances in these verdazyls to get information on the gain of resolution $\Delta\nu/\nu$ when using PMR in DBNO, DMR in diamagnetic solvents and DMR in DBNO. Only qualitative conclusions were possible which can be summarized as follows:

(1) The gain in resolution $\Delta\nu/\nu$ when using DMR instead of PMR was found to be about a factor of 2 to 3 but never 6 as expected from theory.

(2) The gain in resolution when using DBNO as a solvent is one order of magnitude for lines resulting from large coupling constants, but much lower for lines originating from small coupling constants; no significant difference of this solvent effect was found between protons and deuterons. Hence the best possible resolution can be obtained with DMR in DBNO; the maximum gain of $\Delta\nu/\nu$ as compared to PMR in a diamagnetic solvent is about a factor 20.

The difference in coupling constants measured in DBNO and in diamagnetic solvents does not exceed 5%, i.e. it stays well in the range of solvent effects found with diamagnetic solvents.

EXPERIMENTAL

The NMR studies were made with a Bruker-Spectrospin HX-90 MHz high resolution spectrometer. The proton spectra were measured using the broad line technique (30 Hz modulation, phase sensitive detection and linear field sweep). Each spectrum was recorded several times with linear sweep and checked by 2 kHz control distances. The deuterium spectra were measured partly using the broad line technique and partly using the high resolution technique with frequency sweep.

3-*Trideuteromethyl*-1,5-*diphenylformazan*. A mixture of aniline (10·7 g) in H_2O (30 ml) + conc HCl (30 ml) was cooled to 0° and kept at this temp while a soln of $NaNO_2$ (7·9 g) in H_2O (20 ml) was added dropwise with stirring. This diazonium salt soln was added in small portions to a stirred mixture of tetradeuteroacetaldehyde (5 g) in EtOH (200 ml) + phenylhydrazine (12·3 g) + dry NaOAc (35 g) kept at 0°. After 3 hr the reaction mixture was partitioned between benzene and H_2O, the benzene layer was washed 4 times with H_2O and evaporated in vacuum. The residue yielded from benzene-ligroin orange crystals (15·7 g), m.p. 124–125° (dec). (Found: C, 69·88; H + D, 6·86; N, 22·99. $C_{14}H_{11}D_3N_4$ requires: C, 69·68; H + D, 7·09; N, 23·22%).

Pentadeuterophenylhydrazine. A mixture of pentadeuteroaniline (7·5 g) in H_2O (20 ml + conc HCl (20 ml) was cooled to 0° and kept at this temp while a soln of $NaNO_2$ (5·2 g) in H_2O (20 ml was added dropwise with stirring. A soln of $SnCl_2 \cdot 2H_2O$ (40 g) in conc HCl (40 ml) was added in small portions to the stirred diazonium salt soln at 0°. The separated tin salt was removed, dissolved in 4N KOH and the mixture extracted with ether. The ether soln was washed with H_2O and filtered. Evaporation of the solvent in vacuum yielded pentadeuterophenylhydrazine (6 g).

1,1-*Di-pentadeuterophenylazo-neopentane*. A mixture of pentadeuteroaniline (5 g) in H_2O (10 ml) + conc HCl (15 ml) was cooled to 0° and kept at this temp while a soln of $NaNO_2$ (3·5 g) in H_2O (10 ml) was added dropwise with stirring. A soln of pentadeuterophenylhydrazine (6 g) and pivaldehyde (4·3 g) in EtOH (15 ml) was heated to the b.p., cooled, diluted with DMF (80 ml) and pyridine (40 ml) and kept at 0° while the diazonium salt soln was added in small portions with stirring. After 10 min the separated product was collected, yellow prisms (9·5 g), m.p. 94–95° (dec).

3-*t-Butyl*-1,5-*di-pentadeuterophenylformazan*. Crude 1,1-di-pentadeuterophenylazo-neopentane (9·5 g) in DMF (300 ml) + KOMe (2 g) was vigorously stirred for 15 min in an N_2 atmosphere, 2N HCl (25 ml) and H_2O were added and the separated product was collected. From acetone–MeOH dark red crystals (8 g), m.p. 63–64° (dec) were obtained. (Found: C, 70·05; H + D, 9·90; N, 19·45. $C_{17}H_{10}D_{10}N_4$ requires: C, 70·30; H + D, 10·40; N, 19·29%).

3,5-*Dimethyl*-1,5-*diphenylformazan*. 3-Methyl-1,5-diphenylformazan[23] (4 g) in DMF (50 ml) + BaO (10 g) + $Ba(OH)_2 \cdot 8\,H_2O$ (1 g) + MeI (10 ml) was stirred for 3 hr. The mixture was partitioned between benzene and H_2O. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue yielded from MeOH brown crystals (3·2 g), m.p. 77–78° (dec). (Found: C, 71·03; H, 6·11; N, 22·49. $C_{15}H_{16}N_4$ requires: C, 71·40; H, 6·39; N, 22·21%).

3-*Methyl*-5-*trideuteromethyl*-1,5-*diphenylformazan*. 3-Methyl-1,5-diphenylformazan[23] (3 g) in DMF (50 ml) + BaO (10 g) + $Ba(OH)_2 \cdot 8\,H_2O$ (1 g) + trideuteromethyl iodide (5 ml) were treated as above: brown crystals (1·8 g), m.p. 79–80° (dec). (Found: C, 70·54; H + D, 7·18; N, 22·26. $C_{15}H_{13}D_3N_4$ requires: C, 70·56; H + D, 7·50; N, 21·94%).

5-*Methyl*-3-*trideuteromethyl*-1,5-*diphenylformazan*. 3-Trideuteromethyl-1,5-diphenylformazan (5 g) in DMF (100 ml) + BaO (10 g) + $Ba(OH)_2 \cdot 8\,H_2O$ (1 g) + MeI (10 ml) were treated as above: brown crystals (3·9 g), m.p. 77–78° (dec). (Found: C, 70·60; H + D, 7·23; N, 22·10. $C_{15}H_{13}D_3N_4$ requires: C, 70·56; H + D, 7·50; N, 21·94%).

3,5-*Di-trideuteromethyl*-1,5-*diphenylformazan*. 3-Trideuteromethyl-1,5-diphenylformazan (4 g) in DMF (50 ml) + BaO (10 g) + $Ba(OH)_2 \cdot 8\,H_2O$ + trideuteromethyl iodide (5 ml) were treated as above: brown crystals (3·6 g), m.p. 80–81° (dec). (Found: C, 69·76; H + D, 8·72; N, 21·85. $C_{15}H_{10}D_6N_4$ requires: C, 69·73; H + D, 8·58; N, 21·69%).

3-*Methyl*-1,5-*diphenylverdazyl* (VII)

(a) BF_3–ethyl etherate (3 ml) + 38% aqueous formaldehyde (5 ml) in DMF (10 ml) were stirred for 5 min; 3-methyl-1,5-diphenylformazan[23] (2 g) was added and the mixture stirred for 30 min. The mixture was diluted with benzene (150 ml), cooled to 10° and kept at this temp while 2N NaOH was added until the colour of the vigorously stirred mixture had changed to green. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexan–benzene (1 : 1) green fractions, which yielded crystallized twice from MeOH dark green crystals (0·3 g), m.p. 99–100° (dec). (Found: C, 71·43; H, 5·97; N, 22·09. $C_{15}H_{15}N_4$ requires: C, 71·69; H, 6·02; N, 22·29%).

(b) 3,5-Dimethyl-1,5-diphenylformazan (1 g) in DMF (50 ml) was heated to 150° (brown → green) and cooled to room temp. A soln of $FeCl_3 \cdot 6\,H_2O$ (2 g) in 1N Na_2CO_3 (15 ml) was added, the violet mixture was stirred for 1 min and then partitioned between benzene and 0·2 N Na_2CO_3. The benzene layer was washed 4 times with H_2O and evaporated in vacuum. The residue yielded from MeOH dark green crystals (0·35 g), m.p. 98–99° (dec).

6,6-Dideutero-3-methyl-1,5-diphenylverdazyl (VIII)

3-Methyl-5-trideuteromethyl-1,5-diphenylformazan (1 g) was treated as above (VII, procedure b): dark green crystals (0·42 g), m.p. 101–102° (dec). (Found: C, 71·31; H + D, 6·62; N, 22·02. $C_{15}H_{13}D_2N_4$ requires: C, 71·12; H + D, 6·76; N, 22·12%).

3-Trideuteromethyl-1,5-diphenylverdazyl (IX)

(a) 3-Trideuteromethyl-1,5-diphenylformazan (2 g) was treated as above (VII, procedure (a): dark green crystals (0·33 g), m.p. 97–98° (dec).

(b) 5-Methyl-3-trideuteromethyl-1,5-diphenylformazan (1 g) was treated as above (VII, procedure b): dark green crystals (0·38 g), m.p. 98–99° (dec). (Found: C, 70·63; H + D, 6·96; N, 21·89. $C_{15}H_{12}D_3N_4$ requires: C, 70·84; H + D, 7·14; N, 22·03%).

6,6-Dideutero-3-trideuteromethyl-1,5-diphenylverdazyl (X)

3,5-Di-trideuteromethyl-1,5-diphenylformazan (1 g) was treated as above (VII, procedure b): dark green crystals (0·35 g), m.p. 101–102° (dec). (Found: C, 70·19; H + D, 7·94; N, 21·93. $C_{15}H_{10}D_5N_4$ requires: C, 70·28; H + D, 7·86; N, 21·86%).

3,6-Dimethyl-1,5-diphenylverdazyl (XI)

3-Methyl-1,5-diphenylformazan[23] (5 g) in DMF (100 ml) + BaO (10 g) + $Ba(OH)_2 \cdot 8\,H_2O$ (1 g) + EtI (10 ml) were stirred for 5 hr. The mixture was partitioned between benzene and H_2O. The benzene layer was washed 3 times with H_2O and evaporated in vacuum. The residue in DMF (100 ml) was heated to 150° (brown → green) and cooled to room temperature. The soln of $FeCl_3 \cdot 6\,H_2O$ (6 g) in 1N Na_2CO_3 (40 ml) was added, the violet mixture stirred for 1 min and then partitioned between benzene and 0·2 N Na_2CO_3. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue yielded twice crystallized from MeOH green black crystals (750 mg), m.p. 109–110° (dec). (Found: C, 72·41; H, 6·46; N, 20·99. $C_{16}H_{17}N_4$ requires: C, 72·43; H, 6·46; N, 21·12%).

6,6-Dideutero-3-t-butyl-1,5-diphenylverdazyl (XIII)

3-t-Butyl-1,5-diphenylformazan[24] (3 g) in DMF (100 ml) + BaO (5 g) + $Ba(OH)_2 \cdot 8\,H_2O$ (0·1 g) + trideuteromethyl iodide were stirred for 24 hr. The green mixture was partitioned between benzene and H_2O. The benzene layer was washed 2 times with H_2O and evaporated in vacuum. The residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane–benzene (4:1) green fractions, which yielded crystallized from MeOH black needles (0·28 g), m.p. 110–111° (dec). (Found: C, 72·87; H + D, 7·64; N, 18·87. $C_{18}H_{19}D_2N_4$ requires: C, 73·18; H + D, 7·84; N, 18·97%).

3-t-Butyl-1,5-di-pentadeuterophenylverdazyl (XIV)

BF_3–ethyl etherate (5 ml) + 38% aqueous formaldehyde (5 ml) + DMF (20 ml), 5 min; 3-t-butyl-1,5-di-pentadeuterophenylformazan (2 g), 1 hr were treated as above (VII, procedure a). From MeOH green black crystals (0·45 g), m.p. 106–107° (dec). (Found: C, 70·81; H + D, 10·62; N, 18·45. $C_{18}H_{11}D_{10}N_4$ requires: C, 71·25; H + D, 10·29; N, 18·46%).

6-Methyl-3-t-butyl-1,5-diphenylverdazyl (XV)

3-t-Butyl-1,5-diphenylformazan[24] (3 g) + $KHSO_2$ (10 g) + acetaldehyde (2 ml) in DMF (50 ml) were stirred for 3 hr. The mixture was filtered, the filtrate was cooled to 0° and then 2N NaOH was added dropwise until the colour of the mixture changed to green. The mixture was partitioned between benzene and H_2O, the benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane–benzene (1:1) green fractions, which yielded crystallized twice from MeOH black needles (0·68 g), m.p. 82–83° (dec). (Found: C, 74·04; H, 7·39; N, 18·02. $C_{19}H_{23}N_4$ requires: C, 74·23; H, 7·54; N, 18·23%).

6-Deutero-6-trideuteromethyl-1,5-diphenylverdazyl (XVI)

3-t-Butyl-1,5-diphenylformazan[24] (3 g) + $KHSO_4$ (10 g) + tetradeuteroacetaldehyde (2 ml) in DMF (50 ml) were treated as above (XV). From MeOH black crystals (0·52 g), m.p. 88–89 (dec). (Found: C, 73·40; H + D, 8·76; N, 17·87. $C_{19}H_{19}D_4N_4$ requires: C, 73·27; H + D, 8·74; N, 17·99%).

6-Methyl-3-ethoxycarbonyl-1,5-bis(3,5-dichlorophenyl)verdazyl (XVIII)

3-Ethoxycarbonyl-1,5-bis(3,5-dichlorophenyl)formazan[8] (500 mg) in conc ethanolic HCl (30 ml) + BF_3–ethyl etherate (5 ml) + acetaldehyde (2 ml) were stirred for 4 hr. The mixture was diluted with DMF (50 ml) and partitioned between benzene and H_2O. The benzene layer was washed 3 times with H_2O and evaporated in vacuum. The residue yielded crystallized twice from benzene-ligroin green crystals (140 mg), m.p. 121–122° (dec). (Found: C, 47·12; H, 3·37; N, 12·01. $C_{18}H_{15}Cl_4N_4O_2$ requires: C, 46·88; H, 3·28; N, 12·15%).

Hydrogenation of the verdazyls

6,6-Dideutero-3-methyl-1,5-diphenylleucoverdazyl or *3,3-dideutero-6-methyl-2,4-diphenyl-1,2,3,4-tetrahydro-s-tetrazine.* Verdazyl VIII (100 mg) + 5% $Pd/BaSO_4$[7] (100 mg) in benzene (20 ml) were hydrogenated until the solution was colourless. The mixture was filtered, the filtrate evaporated in vacuum. The residue yielded from benzene-ligroin nearly colourless crystals (90 mg), m.p. 122–123° (dec). (Found: C, 71·12; H + D, 7·06; N, 21·90. $C_{15}H_{14}D_2N_4$ requires: C, 70·84; H + D, 7·13; N, 22·03%).

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