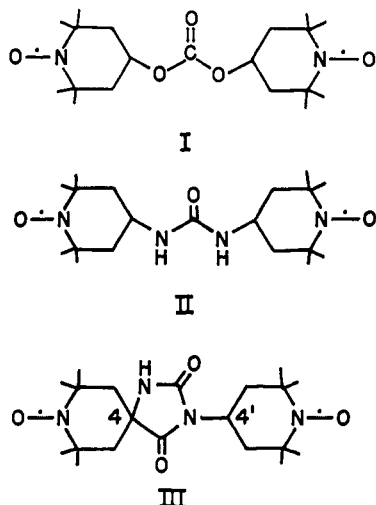


Spin Exchange in Nitroxyl Biradicals

Sir:

We have studied the effects of solvent and temperature on nitroxyl biradicals I,¹ II,¹ and III² and found



some unusual differences in the way these factors influence the magnitude of the exchange energy (J). S resonances³ are clearly observed under most conditions tested and were used to determine the exchange energies listed in Table I.

Table I. Effect of Solvent on Biradicals I-III at 22°

Solvent	Z^a	I		II		III	
		a	J	a	J	a	J
Hexane	60.0	15.2	24.3	15.2	15.8	14.9	43.4
Xylene	63.0	15.2	27.1	15.2	18.6	15.1	26.5
Acetone	65.7	15.6	30.3	15.5	18.2	15.2	19.4
DMF	68.5	16.0	28.9	15.8	18.7	15.4	16.9
DMSO	71.0	15.7	28.8	15.8	17.2	15.4	16.2
MeOH	83.6	16.0	28.7	16.1	17.4	15.8	18.4
H ₂ O	94.6	17.0	38.6	17.1	23.4	16.7	14.8
CHCl ₃	63.2	15.8	35.6	15.9	24.2	15.5	37.4
HOAc	79.2	16.2	34.7	16.4	20.6	15.9	20.3

^a Kosower Z value.⁵

For biradicals I and II in the extended conformation⁴ the distances between the nitroxyl groups and their relative orientations should be essentially identical, but the exchange energy for II is consistently smaller than for I. This comparison is valid down to -60° (in CHCl₃) and therefore is probably not a result of the greater stiffness of II due to amide resonance (see below). For III the nitroxyl groups are held 1–2 Å

(1) E. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. V. Kokhanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 572 (1965).

(2) This compound was originally reported by Joss, *et al.*, *J. Org. Chem.*, **37**, 2015 (1972); as *N*-(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)-*N'*-(1-oxyl-2,2,6,6-tetramethyl-4-methoxycarbonylpiperidyl-4)urea; however, analytical, mass spectral, and nmr data on the compound or amine precursor indicate its correct structure is that of biradical III. The cyclization with loss of methanol is easily envisioned under the reaction conditions used. The weaker set of S resonances noted in the paper by Joss, *et al.*, corresponds exactly to the symmetrical urea II in all solvents, and the S resonances are most likely due to a small amount of this impurity which can easily be formed in the reaction. It should also be noted that the calibration of the esr sweep is incorrect in the Joss paper, which explains the differences in our a and J values.

(3) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967).

(4) H. Lemaire, *J. Chim. Phys.*, **64**, 559 (1967).

closer together than in I or II, and their relative orientation is such that greater overlap of the molecular orbitals containing the unpaired electrons would be expected. Thus, if direct overlap is important in determining the exchange magnitude in those biradicals, then one would expect to observe a much larger exchange in III than in I or II, which is generally not the case. These observations strongly support a participation of the connecting bridge in determining the exchange energy as suggested by Glarum and Marshall.³ They are not consistent, however, with the suggestion that the exchange through the joining structure decreases with the number of σ bonds separating the radical centers,³ since the shortest path for such exchange in III is one bond less than in I or II while the observed exchange can be smaller for III.

The effect of solvent on the exchange energy is similar for biradicals I and II, J tending to increase with increasing solvent polarity (for example, as measured by the Kosower Z value⁵). The hyperfine interaction, a , also changes in a consistent manner with solvent polarity (Table I), and it would seem likely that the solvent dependence of J is related to the changes in electron density distributions indicated by the changes in a .⁶ In contrast to I and II, II shows a decrease in exchange energy with increasing solvent polarity. The greatest variation in J occurs in the solvents hexane, xylene, and chloroform, the other solvents examined all giving similar results, indicating that simple spin density distribution changes in the nitroxyl groups are not solely responsible for the solvent effects. The opposing trends observed for these biradicals considerably complicate the discussion of effects of solvent on the exchange energy. Combined with the observed effects of temperature (see below), these results negate the suggestion that solvent affects the most probable conformations of the biradicals and thereby the exchange.³ Our observations rather seem to emphasize the importance of the connecting bridge in determining J as a function of solvent polarity.

The effect of temperature on exchange in these biradicals is also dependent on the structure and generally reflects the flexibility of the molecules. For I above 30° the exchange energy appears to modulate over a range of values resulting in extreme broadening of the S resonances. This observation has been reported previously and interpreted in terms of increased flexing of the molecule at higher temperatures.³ In CHCl₃, as the temperature is decreased to -60° , the S resonances sharpen progressively, indicating that molecular motion is still important below 0° . In addition, the exchange energy determined from the positions of the S resonances increased with decreasing temperature at a rate of 0.075 G/deg (CHCl₃). In contrast, for II the S resonances begin to broaden at temperatures greater than 100° , yet remain observable up to 200° in xylene. Biradical II thus appears to be considerably less flexible than I, probably due to amide resonance in II. This would indicate that rotation about the carbonyl-oxygen linkage is important in creating the incoherence of J for biradical I at higher temperatures. As the temperature is decreased below 20° , the exchange energy measured from the S resonance positions increases at a rate of

(5) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

(6) H. Hayat and B. L. Silver, *J. Phys. Chem.*, **77**, 72 (1973).

0.025 G/deg (CHCl_3). Unlike biradical I, however, the S resonances tend to broaden slightly with decreasing temperature.

For biradical III, flexing should consist only of limited rotation about the C_4' -N bond and of flexing in the five- and six-membered rings. Accordingly, we observe no broadening of the S resonance lines up to 200° in xylene or down to -60° in carbon disulfide. The twisting amplitude about the C_4' -N bond should be sufficiently large, such that it should have a quite drastic effect on the direct overlap of the unpaired electron distributions. Unless this motion is fast over the entire temperature range examined and therefore results in an average exchange, these observations again indicate that simple direct exchange is of little importance. In contrast to I or II, we observe for III a nearly linear increase in J with increasing temperature of 0.08 G/deg in xylene (20 – 200°), 0.074 G/deg in chloroform (20 – 150°), and 0.092 G/deg in carbon disulfide (-60 to 20°). For all three biradicals studied here, the small changes in J with temperature could be due to rapid conformational changes in the molecules. However, one must also consider the possibility that these changes reflect changes in solvation with temperature, since solvent is important in determining the exchange energy.

These results support the idea that the exchange energy in a biradical is strongly influenced by the chemical nature of the connecting bridge in a manner not simply related to the distance between the nitroxyl groups or their relative orientation. For biradical III the results appear to be inconsistent with either a simple indirect (through bond) or direct (through space) exchange mechanism since one would expect the exchange to increase with the electron density on nitrogen (*i.e.*, with increasing a) as is seen for I and II. The exchange thus seems a complex function of the biradical structure.

Acknowledgment. This work was supported, in part, by the U. S. Atomic Energy Commission.

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Received July 3, 1974

A Total Synthesis of (\pm)-Porantherine

Sir:

Porantherine, the major alkaloid of the low, woody shrub, *Poranthera corymbosa*, has been shown by X-ray crystallography to possess structure 1.^{1,2} We describe here a synthesis of this interesting tetracyclic structure, the first known natural product with a bridged 9b-azaphenylene network.³ The overall plan of synthesis,

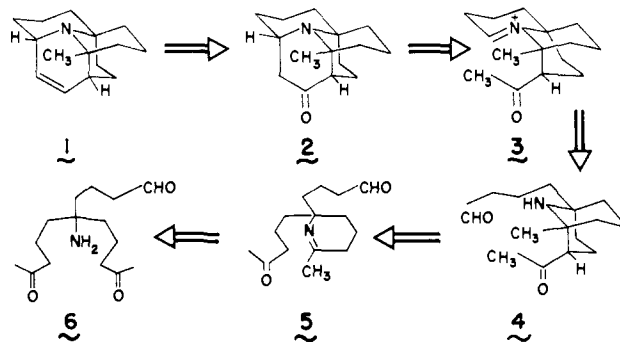
(1) W. A. Denne, S. R. Johns, J. A. Lamberton, and A. McL. Mathieson, *Tetrahedron Lett.*, 3107 (1971).

(2) An ambiguous stereochemical formulation of porantherine given in ref 1 and an erroneous stereo formula appearing in a later publication [W. A. Denne, S. R. Johns, J. A. Lamberton, A. McL. Mathieson, and H. Soares, *Tetrahedron Lett.*, 1767 (1972)] have been superseded by a correction; see Erratum, *ibid.*, 794 (1973).

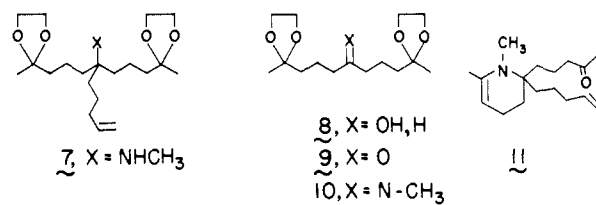
(3) A group of structurally related polycyclic amines has recently been isolated from various insect species. See (a) B. Tursch, D. Dalozé, M. DuPont, J. M. Pasteels, and M. C. Tricot, *Experientia*, 27, 1380 (1971); (b) B. Tursch, D. Dalozé, M. DuPont, C. Hootelé, M. Kaisin,

derived by antithetic (retrosynthetic) analysis,⁴ and unusually simple for such a complex molecule, involves structures 2, 3, 4, 5, and 6 (or equivalents) as key intermediates as shown in Scheme I.

Scheme I



Following this general outline, the synthesis of the symmetric tertiary carbinamine 7 was undertaken. The addition of 2 equiv of the Grignard reagent derived from 5-chloro-2-pentanone ethylene ketal⁵ to ethyl formate in tetrahydrofuran (THF) at reflux gave the desired secondary alcohol 8⁶ (95% yield). Oxidation to the ketone 9 was easily accomplished in 93% yield with 6 equiv of Collins' reagent at room temperature in methylene chloride.⁷ Treatment of the ketone in a sealed tube with 2 equiv of methylamine in toluene containing molecular sieves 4 Å⁸ at 110° for 18 hr afforded a quantitative yield of the imine 10. Finally, four cycles of reaction of 10 with 1-lithio-4-pentene⁹ in benzene at room temperature,¹⁰ gave, after column chromatography on silica gel ($R_f = 0.2$, ether-methanol 1:1), the desired tertiary carbinamine 7 in 65% yield:¹¹ found for 7, $\text{ir}(\text{max})$ (neat) 1635, 1225, and 1060 cm^{-1} ; pmr peaks (CCl_4) at δ 1.25 (s, 6 H, CH_3), 2.2 (b, 3 H, CH_3N), 3.85 (s, 8 H, ketal), and 4.8–6.0 (m, 3 H, vinyl). Extraction of the tertiary carbinamine 7 into



J. M. Pasteels, and D. Zimmermann, *Chimia*, 25, 307 (1971); (c) B. Tursch, D. Dalozé, and C. Hootelé, *ibid.*, 26, 74 (1972); (d) M. C. Tricot, J. M. Pasteels, and B. Tursch, *J. Insect Physiol.*, 18, 499 (1972).

(4) See, for example, E. J. Corey, *Quart. Rev., Chem. Soc.*, 25, 455 (1971), and papers therein cited.

(5) Cl. Feugas and H. Normant, *Bull. Soc. Chim. Fr.*, 1441 (1963).

(6) Satisfactory proton magnetic resonance (pmr) and infrared (ir) spectra and analytical data (exact mass or elemental analysis) have been obtained for all intermediates.

(7) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 35, 4000 (1970).

(8) J. Szmuszkowicz, *Advan. Org. Chem.*, 4, 11 (1963).

(9) The lithium reagent was prepared from 5-bromo-1-pentene and lithium (1% sodium) wire in ether at 0° . The solvent was then evaporated *in vacuo* and replaced by benzene.

(10) In each cycle 1 equiv of the lithium reagent was added to the imine, the reaction was stirred for 1 hr at room temperature and quenched with 1 equiv of 0.4 N HCl in benzene. This sequence, which was repeated four times in the same flask without intermediate operations, was used because of the occurrence of proton transfer to the lithium reagent in competition with $\text{C}=\text{N}$ addition.

(11) (a) J. Heut, *Bull. Soc. Chim. Fr.*, 952 (1964); (b) J. Pornet, *Tetrahedron Lett.*, 967 (1971); (c) L. Miginiac and B. Manze, *Bull. Soc. Chim. Fr.*, 3832 (1968).