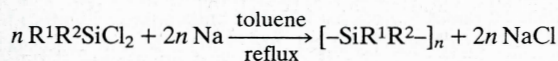


Table 1. Reaction conditions, conversions, and product molecular weights for the polymerization of selected organodichlorosilanes ($R^1R^2SiCl_2$).

Polysilane ^a R^1, R^2	Solvent	Crown ether	Conversion (%)	M_w
Me, Ph	Toluene	No	11	9690
Me, Ph	Toluene	Yes	26	9510
Me, Ph	Ether	No	8	3700
Me, Ph	Ether	Yes	99 (55 ^b)	65950
Ph, Ph	Toluene	No	36	
Ph, Ph	Ether	Yes	81	
Ph, <i>p</i> -Tol	Ether	Yes	40	
Me, <i>p</i> -Tol	Toluene	Yes	8	4340
Me, <i>p</i> -Tol	Ether	No	1	3400
Me, <i>p</i> -Tol	Ether	Yes	66 (25 ^b)	7030
n-Hex n-Hex	Ether	Yes	22 (9 ^b)	23800

^a *p*-Tol = *p*-MeC₆H₄; n-Hex = n-hexyl. ^b Yield taken from reference 1 for syntheses in toluene without any additive.



Scheme 1

consequence the yields of desired polymer are usually only in the region of 9–55%¹ and are difficult to reproduce. Recently it has been shown^{5,6} that in the presence of catalytic amounts of a crown ether, better reproducibility of polymer yields can be achieved with molecular weight distributions tending to the monomodal. Furthermore, for the polymerisation of dichloro-di-n-heptylsilane in toluene the polymer yield was higher when 15-crown-5 rather than heptane or diglyme was added to the reaction mixture. However, in the case of the polymerization of dichloromethylphenylsilane,⁵ the presence of the crown ether did not alter the proportion of cyclic to polymeric product, even though the yield of the latter was increased to about 60%.

The polymerisations of methylphenyl-, methyltolyl-, diphenyl-, phenyltolyl-, and di-n-hexyl-silane and of diphenylgermane have been investigated to establish the optimum reaction conditions for the formation of high yields of high molecular weight products. The results are given in Table 1. Molecular weights were determined as polystyrene equivalents in tetrahydrofuran (THF) solution using size exclusion chromatography. In the case of the otherwise intractable polydiarylsilanes and polydiphenylgermane, slight solubility for this purpose was achieved in boiling THF but the resultant data are considered to be unreliable and so are not quoted.

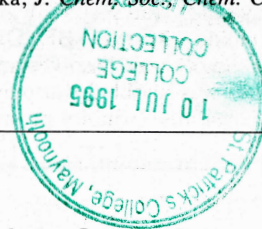
The reactions of dichloromethylphenylsilane with sodium sand in refluxing toluene, in refluxing toluene in the presence of 15-crown-5, and in refluxing diethyl ether all gave low yields of a low molecular weight polymer. On the other hand the reaction using diethyl ether as the reflux medium in the presence of 15-crown-5 resulted in an almost quantitative yield of product consisting of 12% of cyclic material (removed by extraction in hexane) and 88% of high molecular weight polymer which was readily soluble in THF. Similar trends are observable for the other polymerizations including those of the dichlorodiarylsilanes.

The results suggest that high yields of polysilanes can better be achieved from the interaction of a dichlorosilane and sodium sand in the presence of 15-crown-5 at the low refluxing temperature attainable using diethyl ether. Polydiphenylgermane was obtained in 74% yield under these conditions.

Received, 25th April 1990; Com. 0/01841D

References

- 1 R. West, *J. Organomet. Chem.*, 1986, **300**, 327.
- 2 R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359.
- 3 S. Yajima, J. Hayashi, and M. Omori, *Chem. Lett.*, 1975, 931.
- 4 R. D. Miller, D. Hofer, D. R. McKean, and C. G. Wilson, 'Materials for Microlithography,' American Chemical Society Symposium Series No. 266, Washington, DC, 1984, p. 293.
- 5 S. Gauthier and D. J. Worsfold, *Macromolecules*, 1989, **22**, 2213.
- 6 M. Fujino and H. Isaka, *J. Chem. Soc., Chem. Commun.*, 1989, 466.



Complexes of a New Mononucleating Cage Ligand; Livelier than Sepulchrates?

Josie Hunter,^{a,b} Jane Nelson,^{a,b} Charlie Harding,^b Malachy McCann,^c and Vickie McKee^d

^a Chemistry Department, Queen's University, Belfast BT7 5AG, UK

^b Open University, Milton Keynes MK7 6AA, UK

^c Chemistry Department, St Patrick's College, Maynooth, Ireland

^d Chemistry Department, University of Canterbury, Christchurch 1, New Zealand

A new polyaza cryptand L¹, easily made by Schiff's base condensation using Group 2 ions, may be transmetallated with first transition series ions to give cryptates which electrochemical investigations show to have relatively stable +1 oxidation states; a preliminary X-ray crystallographic study of the Co^{II} cryptate is reported.

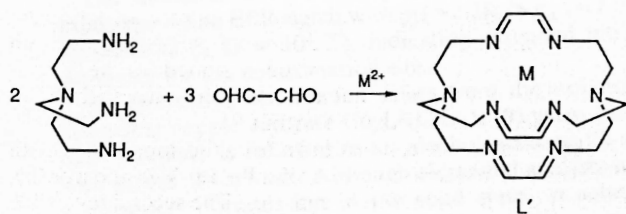
The elegant and comprehensive work of Sargeson *et al.*¹ on mononucleating cage ligands of the sep- and sar-type is subject to one significant limitation; {sep (sepulchrates) = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane, sar (sarcophagine) = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane}. Because the synthesis uses a kinetically inert metal ion as

template, subsequent removal of this metal ion presents difficulty. We have developed² a synthetic approach to cryptand ligands, involving the use of kinetically labile template ions, which avoids this difficulty. The [2 + 3] condensation of the tripod amine tris(2-ethylamino)amine with glyoxal using Group 2 metal ion templates (Scheme 1)

Table 1. Spectroscopic, magnetic, and electrochemical^{c-d} properties of the cryptates.

Compound	π-π* or charge-transfer bands ^e		d-d bands ^g λ _{max} /cm ⁻¹ (ε)	μ/μ _B		E/mV					
	λ _{max} /cm ⁻¹	ε/dm ³ mol ⁻¹ cm ⁻¹		293 K	93 K	E ^I _{1/2}		E ^{II} _{1/2}		E ^{III} _{1/2}	
						(ΔE)	(ΔE)	(ΔE)	(ΔE)		
[CaL ^I](BPh ₄) ₂ ^h (1)	35 710	1800	—	—	—	a		a		a	
[MnL ^I](BPh ₄) ₂ ⁱ (2)	29 400	930	—	5.99	5.98	+1350 ^b	Irr.	-987	76	-1276	76
[FeL ^I](BPh ₄) ₂ ⁱ (3)	23 100	2300	—	0.95	0.40	+714 ^b	Irr.	-962	61	-1332	77
	17 400	5600									
[FeL ^I](ClO ₄) ₂ ^j (4)	23 100	1500	—	Dia.	Dia.	+810	127	-983	61	-1349	61
	17 460	3800									
[CoL ^I](BPh ₄) ₂ ⁱ (5)	26 200	1900	11 430 (19)	4.30	4.20	+227	207	-847	87	-1402	87
[CoL ^I](ClO ₄) ₂ ^j (6)	26 430	1600	11 100 (5)	4.43	3.95	+740 ^e	Irr.	-815	61	-1371	77
						+131 ^f					
[NiL ^I](BPh ₄) ₂ ⁱ (7)	33 200	1600	12 500 (18)	3.04	3.01	+1166	Irr.	-1105	61	-1838	91
	25 900	1400									
[CuL ^I](ClO ₄) ₂ ·4H ₂ O ^j (8)	35 600	2700	15 500 (120)	1.86	1.61	+1216	Irr.	+282	77	-1197	96
	24 300	2150									

^a No electrochemical activity in this range. ^b Poorly defined oxidation wave, partly obscured by counterion or solvent process. ^c Scan rate 50 mV s⁻¹; E_{1/2} ferrocenium/ferrocene +362 mV, ΔE 92 mV vs. AgCl. ^d 10⁻³ M in dmf, 0.1 M Et₄NClO₄. ^e Anodic component. ^f Cathodic component. ^g MeCN solution. ^h Made by template synthesis at 40–50°C in EtOH. ⁱ Made by transmetallation of (1) or its Sr analogue with M²⁺ (M = Mn, Fe, Co, Ni, or Cu) in MeCN–EtOH. ^j Made by anion exchange of (1) with AgClO₄ followed by transmetallation with M(ClO₄)₂.

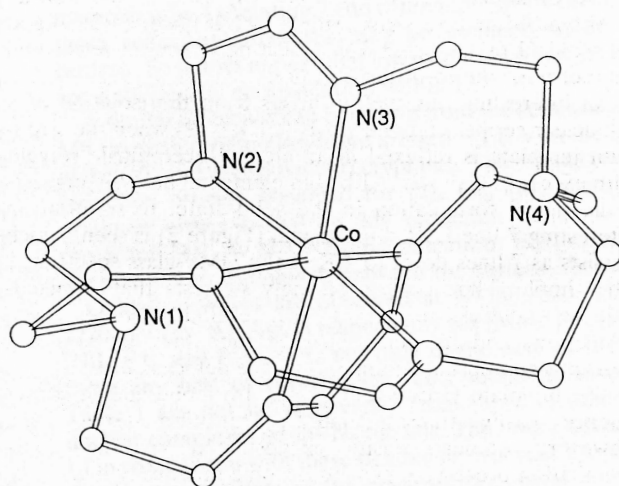
**Scheme 1**

results in formation of the hexaimino macrobicyclic ligand L^I in good yield.

The template ion may then be easily removed by transmetallation with *e.g.* first transition series ions to give mononuclear complexes (Table 1).

Crystals of CoL^I(ClO₄)₂ have been studied by X-ray diffraction. The crystals show intimate twinning which precluded accurate determinations of bond lengths and angles; nevertheless the main features of the structure are clear.† The structure of the cation is shown in Figure 1, the cobalt atom and the two bridgehead nitrogen atoms lie on a crystallographic 3-fold axis. The metal is co-ordinated to all six imino donors (only two of which are crystallographically independent) and has D₃ symmetry. The Co–N (imine) distances are similar to those in the analogous [Co(sep)]²⁺ cryptate.³ The unco-ordinated bridgehead amino N lies ≈3 Å from the metal ion within a near planar arrangement of adjacent methylene carbons, suggesting near sp² hybridization of tertiary amine nitrogens, as observed⁴ in [Ni(sep)]²⁺. The methylene caps are staggered, with a twist angle φ of ≈55°.

The observed disorder–twinning chiefly affects the di-imino links and therefore only tentative conclusions are possible. It appears that these links are oblique rather than parallel. The perchlorate anions lie with one Cl–O bond along a 3-fold axis and they do not show any interactions with the cations.

**Figure 1.** Preliminary crystal structure of [CoL^I]²⁺.

Although the tail of the broad and intense ligand-to-metal charge transfer (LMCT) absorption dominates the visible region of the electronic spectrum, low intensity bands around 11 000 and 12 000 cm⁻¹ are, in the case of (5)/(6) and (7), seen and attributed to the lowest energy transition allowed in approximate O_h symmetry for Co^{II} and Ni^{II} respectively. Isomorphous powder patterns for (5) and (7) corroborate the spectral evidence. However (2) and (3) are not isostructural with (5)/(7) nor with each other reflecting presumably the varying influence of ligand field stabilising energy (LFSE) effects in favouring trigonal antiprismatic over the less strained trigonal pyramidal geometry in the order Fe²⁺ > Co²⁺ > Mn²⁺.

All the mononuclear cryptates, as expected, show little temperature-dependence of magnetic moment with evidence of some deviation from regular octahedral geometry in the low values recorded for (5) and (6). The Fe^{II} cryptates (3) and (4)

† Solved in the hexagonal space group P6₃, a = 9.164, c = 17.185 Å, current R = 0.11. Full details will be published elsewhere.

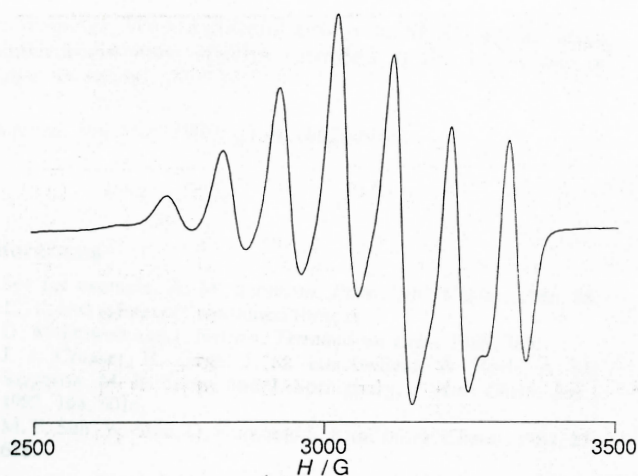


Figure 2. ESR spectrum of (9) as a dimethylformamide (dmf) glass at 113 K.

however, are in the 1A_g low spin state at ambient temperature, suggesting that distortion from octahedral geometry, in the case of Fe^{II} , is not large.

The mononuclear Cu^{II} complex (8) exhibits the normal axial-type 4-line ESR signal with $g_{||} (\approx 2.28) > g_{\perp} (\approx 2.07)$ and $A_{||} \approx 143$ G (1 G = 10^4 T), indicating extended tetragonal geometry for the co-ordination site.

An interesting observation arises from the isolation of a bi-nuclear copper cryptate $Cu_2L^1(ClO_4)_4$ (9) when the strontium template is refluxed in an alcohol-acetonitrile solvent with excess of Cu^{II} salt. Although elemental analysis suggests a dicopper II formulation in the solid state, in solution an interesting 7-line ESR $g = 2$ signal (Figure 2) is seen, which persists as 7 lines down to 4 K in the DMF-glass spectrum.† The simple 7-line pattern strongly suggests that a mixed-valence Cu^{II}/Cu^I species has been formed *via* redox transformation, and its persistence to such low temperatures indicates an unusual degree of valence delocalization.

The template Group 2 cryptates are labile and in consequence easily transmetallated. Transition series ions, however, although easily encapsulated *via* the transmetallation process, appear to become kinetically inert once encapsulated; treatment of $[CoL^1]^{2+}$ with NaCN (aq.) fails to generate a $Co(CN)_2$ precipitate during several weeks. The aqueous stability of (6) is remarkable for a Schiff's base complex; water is indeed one of the best recrystallisation solvents for this complex.

The encapsulated transition series ions may thus be expected to function as sterically protected kinetically inert redox reagents of the 'innocent' kind. In contrast to Sargeson's hexamino cryptands,⁵ our hexaimino donor set should favour to some degree the adoption of low oxidation states. The +3/+2 couples for cobalt complexes of sar and sep are seen at -200 and -220 mV respectively (*vs.* standard calomel electrode, SCE); *i.e.* some 400 mV less positive than the analogous quasi-reversible couple in (5) (Figure 3). The +2/+1 reduction for cobalt sar and sep complexes is irreversible and occurs at very negative (*ca.* -2000 mV) potential, whereas, as Figure 3 shows, reversible reductions at -830 and ≈ -1380 mV (*vs.* Ag/AgCl) are characteristic of $[CoL^1]^{2+}$. On

† The lability of this species at ambient deters us from reporting its apparent solution properties at this stage.

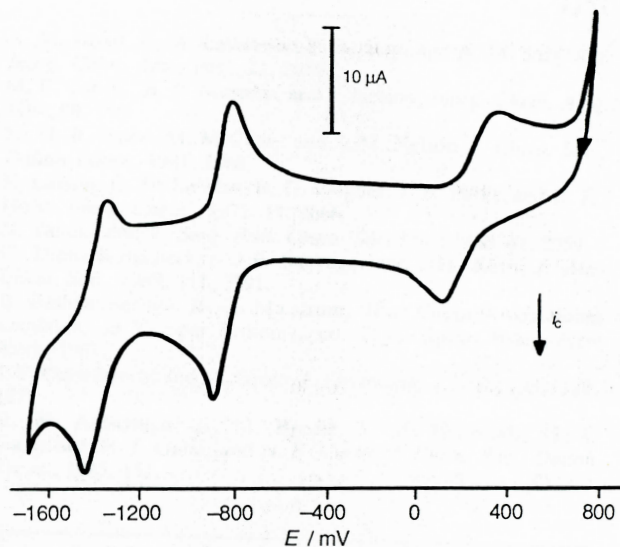


Figure 3. Cyclic voltammograms of (5) in dmf; scan rate 50 mV s^{-1} .

the basis of related work with complexes of macrocyclic,^{6,7} macrobicyclic,⁸ chelating,⁹ and catenand¹⁰ sp^2 -N donors, both these reduction processes may be assumed to be metal-centred. So it does appear that low oxidation states such as Co^I are stabilised by encapsulation within L^1 .

A similar inference can be drawn from the appearance of an M^{II} reversible reduction wave around -1.0 V in the iron(II), nickel(II), and manganese(II) cryptates. The second reversible reduction process observed for (2), (3), (4), and (7) may originate either in $M^I \rightarrow M^0$ reduction or a metal ion-promoted $M^IL \rightarrow M^IL^-$ ligand reduction. ESR experiments are planned to distinguish between the various alternatives.

Oxidation waves are observed at +1350, 820, 1170, and 1220 mV (*vs.* Ag/AgCl) respectively for $[MnL^1]^{2+}$, $[FeL^1]^{2+}$, $[NiL^1]^{2+}$, and $[CuL^1]^{2+}$, but only in the case of $[FeL^1]^{2+}$ is there any hint of reversibility. The potentials recorded in Table 1 are not far removed^{6,7} from those of other mononuclear complexes of sp^2 -N₆ ligands. The major advantage of L^1 in comparison with these flexible macrocyclic ligands lies in the kinetic inertness of the encapsulated metal ion and the enhanced chemical stability towards *e.g.* hydrolysis of the cryptand ligand.

The positive potential recorded for the +2/+1 reduction in (8) is interesting. Such positive potentials of the order of those seen in blue copper proteins¹¹ are commonly associated with a co-ordination environment which favours tetrahedral geometry¹⁰ and/or involves sulphur donors.¹² There are advantages to be gained from avoiding the use of S-donors where copper redox processes are involved because such ligands¹³ are often found to be oxidisable at the sulphur site. The tetrahedral geometry enforced on the transition ion site, in Sauvage's innovative strategy, dispenses with the need for S-donors, but for some purposes may overenhance stability of the low oxidation state. We believe that the new copper cryptates described above, which show the borderline +2/+1 stability associated with efficient copper redox catalysis, may prove to be of value as chemically robust redox reagents for effecting mild redox transformations.

We thank DENI for support (to J. H.), and the SERC for contributing to the cost of a Faraday balance and PE λ9

spectrometer. We are grateful also to the SERC for fast-atom bombardment mass spectra recorded at the University of Wales, Swansea.

Received, 9th May 1990; Com. 0102049D

References

- 1 See for example, A. M. Sargeson, *Pure Appl. Chem.*, 1986, **58**, 1511, and references contained therein.
- 2 D. McDowell and J. Nelson, *Tetrahedron Lett.*, 1988, 385.
- 3 J. J. Creaser, R. Gene, J. M. Harrowfield, A. Herlt, A. M. Sargeson, M. R. Snow, and J. Springborg, *J. Am. Chem. Soc.*, 1982, **104**, 6016.
- 4 M. P. Suh, W. Shin, D. Kim, and S. Kim, *Inorg. Chem.*, 1984, **23**, 618.

- 5 A. M. Bond, G. A. Lawrance, P. A. Ray, and A. M. Sargeson, *Inorg. Chim. Acta*, 1983, **22**, 2010.
- 6 M. F. Cabral, B. P. Murphy, and J. Nelson, *Inorg. Chem. Acta*, 1984, **90**, 169.
- 7 M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1868.
- 8 E. Larson, G. N. La Mar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2666.
- 9 N. Tanaka and Y. Sato, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2059.
- 10 C. Dietrich-Buchecker, J.-P. Sauvage, and J.-M. Kern, *J. Am. Chem. Soc.*, 1989, **111**, 7791.
- 11 B. Reihammer and B. G. Malstrom, 'Blue Copper—containing Oxidases,' in 'Copper Proteins,' ed. T. G. Spiro, Wiley, New York, 1981.
- 12 J. P. Gisselbrecht and M. Gross, *J. Electroanal. Chem.*, 1981, **127**, 127.
- 13 E. W. Ainscough, A. M. Brodie, J. M. Husbands, G. J. Gainsford, E. J. Gabe, and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1985, 151.

Novel Synthesis of Indolizines

Nagatoshi Nishiwaki, Kiyonori Furuta, Mitsuo Komatsu, and Yoshiki Ohshiro*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

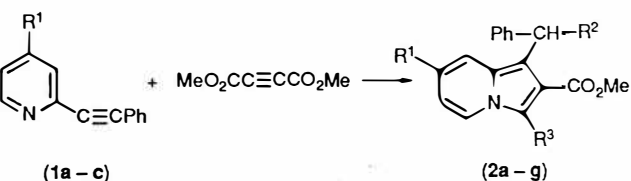
2-Phenylethynylpyridine reacted with dimethyl acetylenedicarboxylate (DMAD) in the presence of a proton source such as an alcohol to give indolizines having methoxycarbonyl groups at the 2- or 2,3-positions in high yields.

We previously reported the direct ethynylation of pyridines by the Reissert-Henze type reaction.¹ In order to use pyridines having an ethynyl group in the synthesis of bicyclic pyridines, we studied the reaction of acetylenylpyridines with dimethyl acetylenedicarboxylate (DMAD). Acheson and Bridson had tried this reaction, but they obtained only unidentified materials.² In contrast, we have now found that this reaction gave indolizine derivatives.

A benzene solution (10 ml) of 2-phenylethynylpyridine (**1a**) (1 mmol), MeOH (20 mmol), and DMAD (2 mmol) was stirred at room temperature for one day. The mixture was concentrated and chromatographed (SiO₂; hexane-AcOEt, 95:5) to give 1-(α -methoxybenzyl)-2-methoxycarbonylindolizine (**2a**) as a pale-yellow oil in 85% yield.

The structure of (**2a**) was determined from spectral and analytical data.[†] Measurement of ¹H-¹H 2D NMR nuclear Overhauser enhancements (NOEs) supported the structure; the correlations observed are shown in Figure 1. Since it is known that quinolizine derivatives may be obtained from pyridine and DMAD,³ the quinolizine (**3**) is an alternative structure for the product. However, this possibility was easily excluded by observation of a doublet sp³ carbon signal at δ 74.3 in the ¹³C NMR spectrum.

Other dipolarophiles such as methyl acetylenemono-



Scheme 1. Conditions: Additive, benzene, room temp., 1 day.

carboxylate, dimethyl maleate, and *N*-phenylmaleimide were not reactive under similar conditions. The present method was also applicable to substituted acetylenylpyridines. The acetylenylpyridines (**1b**) and (**1c**) gave the corresponding indolizine derivatives (**2e**) and (**2f**) in moderate yields.

In the absence of an alcohol, the reaction of the pyridine (**1a**) with DMAD in benzene or tetrahydrofuran (THF) became more complicated. Thus, several alcohols were studied as a proton source, which seems to be essential for this reaction. With EtOH and PrⁱOH, the reaction proceeded similarly and formed the corresponding products (**2b**) and (**2c**), respectively. In the case of Bu^tOH, demethoxycarbonylation at the 3-position did not occur and (**2d**) was isolated. When MeOD was used instead of MeOH, the product (**4**) deuteriated at the benzyl position and the 3-position of the indolizine skeleton was obtained in 98% yield, showing that these two protons come from the alcohol. It is noteworthy that the reaction in the presence of dimethyl malonate instead of an alcohol resulted in carbon-carbon bond formation at the benzyl position and gave the indolizine (**2g**).

On heating the 2,3-bis(methoxycarbonyl) derivative (**2d**) in MeOH, substitution at the benzyl position occurred to give the analogue (**2h**). Generation of MeO⁻ in the reaction of phenanthridine and DMAD in MeOH has been reported,⁴ but further treatment of (**2h**) with MeONa (2 equiv.) caused no

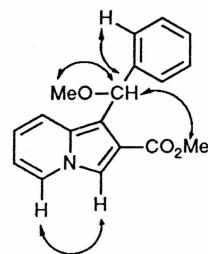


Figure 1. NOE correlations in (**2a**).

[†] All indolizine derivatives gave satisfactory spectral and analytical data.