bonding orbital. That the long wavelength band is correctly assigned as ligand to metal charge transfer is indicated by the shift produced on substituting *trans*-NH_3 by isonicotinamide. Taking into account the increase in reduction potential attending this change the new band position is calculated as 750 nm, to be compared with the observed 772 nm. The observations made on replacing NH_3 trans to sulfur by isonicotinamide demonstrate that the intensity of long wavelength band in the complex of the eight-membered ring is very sensitive to this change. The lone-pair interactions are also very sensitive to substitution on the sulfur atoms. Thus, both binuclear species, ([3,2] and [3,3]) show only a single band in the visible, the positions being nearly the same for both. For the [3,3] species, λ_{max} is registered at 510 nm with ϵ 7.0×10^2 M^{-1} cm^{-1}. The diminution in the splitting in the binuclear complexes can be ascribed to the contraction of the sulfur orbitals by the cationic charges and, on this basis, the position of the single band can be taken as an approximate measure of the center of gravity of the orbitals when they are unaffected by the lone pair interactions.

The second observation which is significant for the issue of through-space interaction is the much higher intensity recorded for the intervalence transition of the mixed valence complex based on the eight-membered ring compared to the six-membered ring (see Figure 3). Effects transmitted through the σ-bond systems are expected to be much weaker in the former than in the latter case, and thus the higher intensity observed for the former suggests a through-space mechanism for the interaction in the case of the eight-membered ring. Presumably, the stable conformation of the eight-membered ring allows for better overlap of the sulfur lone pairs than is the case for the six-membered ring.

If the general correlation between rates of intramolecular electron transfer (Ru(II)-Co(III)) and the intensity of the intervalence transition for the Ru(III)-Ru(II) mixed valence molecules with the same bridging groups[6,7] carries over to the present system, the results suggest that the through-space contact in the eight-membered ring is sufficient to provide for virtually adiabatic electron transfer between the metal ions.

Acknowledgment. Support of this research under Grant GM 13868 is gratefully acknowledged. The procedure for the preparation of 1,5-dithiocane was kindly provided by W. K. Musker.

References and Notes

(1) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976).
(2) W. K. Musker and P. B. Roush, *J. Am. Chem. Soc.*, **98**, 6745 (1976).
(3) C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976).
(4) The ion $(NH_3)_5RuS(CH_3)_2^{2+}$ was prepared both by the method of Kuehn and Taube in ref 3 of by the general method used for the synthesis of I and II.
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Preparative Nucleophilic Substitution with "Betylates". Substrate Phase Transfer and Substrate-Reagent Ion-Pair Reactions[1,2]

Sir:

We wish to point to the synthetic value of ammonioalkanesulfonate esters ("betylates")[3] as intermediates in the overall reaction ROH + Nu → RNu as in

$$\mathrm{ROH} \rightarrow \underset{\mathbf{1}\ (n = 2;\ \mathrm{R'} = \mathrm{Me\ or\ H})}{\mathrm{ROSO_2(CH_2)}_n\mathrm{N^+Me_2R'X^-}} \xrightarrow{\mathrm{Nu^-}\ (\text{or Nu})} \underset{\mathbf{2}}{\mathrm{RNu} + \mathrm{\bar{O}_3S(CH_2)}n\mathrm{N^+Me_2R'}} \quad (1)$$

and at the same time to call attention to two useful ways of facilitating reaction between a lipophilic substrate and a hydrophilic reagent. As may be seen from Table I, betylates work well with a remarkably wide array of nucleophiles, substrates, and solvent systems; the procedures are characterized by mild conditions, easy workup, and the formation of clean products with generally good yields.[4] Noteworthy are (a) the use of an aqueous medium with substrates bearing large hydrophobic alkyl groups (e.g., 1-docosyl), and (b) the formation of the corresponding esters with such feeble nucleophiles as perchlorate and triflate anions.

[2]Betylates (**1**, $n = 2$) are made[4,5] from the alcohol via the ethenesulfonate ester (**3**) in overall yields of ~90–95%. In a homogeneous system (acetone:H_2O) [2]betylates are about as reactive to nucleophiles (e.g., N_3^-) as trifluoroethanesulfonates,[6] but in an aqueous suspension or a CH_2Cl_2:H_2O system [2]betylates react as much as 10^5 times more quickly. One specific limitation of the [2]betylate grouping stems from the ease with which bases convert it back to ethenesulfonate (**3**), sometimes followed by Michael addition to form **4**.

$$\underset{\mathbf{1}(n = 2)}{\mathrm{ROSO_2CH_2CH_2N^+R'_3\ X^-}} \xrightarrow{\text{base}} \underset{\mathbf{3}}{\mathrm{ROSO_2CH{=}CH_2}} + \mathrm{R'_3N}$$

$$\mathrm{ROSO_2CH_2CH_2Nu}$$
4

[3]Betylates (**1**, $n = 3$), however (which are obtained as shown[7] in Scheme I), show no tendency to eliminate the trialkylammonio group under such conditions and are converted in good yields to the substitution products with both basic and nonbasic nucleophiles. [3]Betylates react about 10 times more slowly than [2]betylates.

In addition to providing what we believe to be a useful and general synthetic procedure, the reactions of betylates illustrate two powerful methods for dealing with the general synthetic problem of inducing reaction between a lipophilic substrate and a hydrophilic reagent.[9] One method, "substrate phase transfer", has three logically distinct steps, (i) attachment of a hydrophilic group to the original substrate (ROH → **1**, in the present case), (ii) reaction in an aqueous medium, and (iii) removal of the hydrophilic group. In practice these conceptual steps need not be separate processes, steps ii and iii in the present examples occur in the same reaction. Solid-liquid

Scheme I

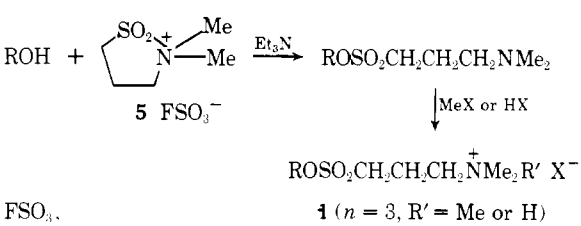

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Table I. Reaction of [2]- and [3]Betylates with Nucleophiles

Procedure[a]	Substrate: Betylate	(mmol)	R	X^-	Reagent	Conditions, medium (T, °C, time)	Product	% yield[b]
A	$Me_3N^+(CH_2)_2$-SO_2OR	(11)	1-Butyl	FSO_3^-	KSCN	H_2O (25, 2 h)	RSCN	91
A		(8)	1-Butyl	FSO_3^-	Na_2SO_3	H_2O (25, 1 h)	$RSO_3^-Na^+$	(80)
C4	$HMe_2N^+(CH_2)_2$-SO_2OR	(22)	Neopentyl	I^-	None	DMF (120–130, 2 h)[c]	RI	68
B	$Me_3N^+(CH_2)_2$-SO_2OR	(0.5)	1-Octyl	ClO_4^-	KSCN	$CHCl_3$:H_2O (25, 24 h)	RSCN	88
B		(0.5)	1-Octyl	ClO_4^-	$(NH_2)_2C{=}S$	PhH:H_2O (25, 21.5 h)	$[RSC(NH_2)_2]^+ClO_4^-$	75
C1		(0.25)	1-Octyl	ClO_4^-	None	$PhCH_3$ (110, 1.5 h)	$ROClO_3$	92
C3		(0.5)	1-Octyl	I^-	None	$CHCl_3$ (61, 0.25 h)	RI	70
B		(0.5)	2-Octyl	FSO_3^-	NaN_3 (satd)	$CHCl_3$ (25, 0.25 h)	RN_3	85
A		(2.0)	1-Hexadecyl	FSO_3^-	NaN_3 (satd)	H_2O (25, 4 h)	RN_3	90
A		(1.0)	1-Hexadecyl	FSO_3^-	KBr	H_2O (25, 5 h)	RBr	90
A		(0.5)	1-Hexadecyl	FSO_3^-	KCN	H_2O (25, 60 h)	$ROSO_2CH_2CH_2CN$	90
B		(0.5)	1-Hexadecyl	FSO_3^-	NaCl	CH_2Cl_2:H_2O (50, 18 h)	RCl	80
B		(0.5)	1-Hexadecyl	FSO_3^-	KNO_3	CH_2Cl_2:H_2O (50, 16 h)	$RONO_2$	65
B		(0.5)	1-Hexadecyl	FSO_3^-	$(NH_2)_2C{=}S$	PhH:H_2O (25, 1 h)	$[RSC(NH_2)_2]^+$-FSO_3^-	75
B		(0.25)	1-Hexadecyl	FSO_3^-	NaOAc	CH_2Cl_2:H_2O (25, 2.5 h)	$ROSO_2CH{=}CH_2$	90
B		(0.25)	1-Hexadecyl	FSO_3^-	NaSH	CH_2Cl_2:H_2O (25, 0.25 h)	$ROSO_2CH{=}CH_2$	60
D		(0.25)	1-Hexadecyl	FSO_3^-	NaOEt	EtOH:PhH (25, 3 h)	$ROSO_2CH_2CH_2OEt$	55
C1		(0.4)	1-Hexadecyl	FSO_3^-	None	$PhCH_3$ (110, 0.25 h)	$ROSO_2OR$	90
C1		(0.4)	1-Hexadecyl	CH_3-SO_3^-	None	$PhCH_3$ (110, 1 h)	$ROSO_2CH_3$	74
C1		(0.2)	1-Hexadecyl	ClO_4^-	None	$PhCH_3$ (110, 1.5 h)	$ROClO_3$	100
C1		(0.2)	1-Hexadecyl	CF_3-SO_3^-	None	$PhCH_3$ (110, 2 h)	$ROSO_2CF_3$	67
C3		(0.4)	1-Hexadecyl	SCN^-	None	$CHCl_3$ (61, 0.5 h)	RSCN	77
C4	$HMe_2N^+(CH_2)_2$-SO_2OR	(0.5)	1-Hexadecyl	Cl^-	None	PhH (81, 0.25 h)	RCl	100
C4		(0.5)	1-Hexadecyl	I^-	None	PhH (81, 0.5 h)	RI	92
A	$Me_3N^+(CH_2)_2$-SO_2OR	(0.2)	1-Docosyl	FSO_3^-	KBr	H_2O (25, 3.5 h)	RBr	74
B		(0.2)	1-Docosyl	FSO_3^-	NaN_3 (satd)	PhH:H_2O (25, 1 h)	RN_3	77
B	$Me_3N^+(CH_2)_3$-SO_2OR	(1)	1-Butyl	FSO_3^-	Imidazole	$CHCl_3$:H_2O (25, 18 h)	1-R-imidazole	84
B		(0.5)	1-Hexadecyl	FSO_3^-	NaN_3	CH_2Cl_2:H_2O (25, 24 h)	RN_3	100
B		(0.5)	1-Hexadecyl	FSO_3^-	NaSPh	PhH:H_2O (25, 18 h)	RSPh	85
B		(0.5)	1-Hexadecyl	FSO_3^-	NaCN	PhH:H_2O (25, 72 h)	RCN	95
B		(0.5)	1-Hexadecyl	FSO_3^-	NaBr	PhH:H_2O (25, 48 h)	RBr	95
C1		(0.5)	1-Hexadecyl	FSO_3^-	None	$PhCH_3$ (110, 4.5 h)	$ROSO_2OR$	85
C2		(0.6)	1-Hexadecyl	Cl^-	None	$PhCH_3$ (110, 2 h)	RCl	95
C2		(0.6)	1-Hexadecyl	CN^-	None	$PhCH_3$ (110, 2.5 h)	RCN	(60)
C2		(0.5)	1-Hexadecyl	F^-	None	$PhCH_3$ (110, 84 h)	RF	(47)
C4	$HMe_2N^+(CH_2)_3$-SO_2OR	(0.6)	1-Hexadecyl	Br^-	None	$PhCH_3$ (110, 2 h)	RBr	(80)
B	$Me_3N^+(CH_2)_3$-SO_2OR	(1.0)	2-Octyl	FSO_3^-	NaSPh	$PhCH_3$ (25, 18 h)	RSPh	60

[a] Procedures. A: a suspension (or solution) of the substrate is stirred with an aqueous solution of the reagent (in tenfold excess). B: a solution of the substrate in the organic phase is stirred with an aqueous solution of the reagent (tenfold excess except as otherwise noted). Typical conditions for 0.5 mmol of the substrate include 10 mL of each phase in a 50-mL round-bottomed flask stirred by a magnetic stirrer at ~500 rpm (i.e., slowly enough to avoid thick emulsions). C1: the substrate was simply heated as specified. Procedures C2 to C4 have the same final step as C1 and differ in that the substrates were obtained as follows: C2, by ion exchange of a methanolic solution of the FSO_3^- salt on Rexyn 201 or 202 resin and evaporation of solvent; C3, by stirring the FSO_3^- or ClO_4^- salt in CH_2Cl_2 with an aqueous solution of excess K^+Nu^- for 15–30 min and then separating the organic layer; C4, by adding excess HNu to a CH_2Cl_2 solution of $Me_2N(CH_2)_nSO_2OR$ and then evaporating the solvent. [b] Yields without parentheses refer to isolated yields of products judged pure by NMR and (or) IR spectra. Yields within parentheses have been estimated from NMR spectra. [c] $Me_2N(CH_2)_2SO_2O$-neopentyl (22 mmol) mixed with aqueous 57% HI (33 equiv, 1.5 mL) in DMF (25 mL) and refluxed.

substrate phase transfer is believed to occur in the reactions carried out as aqueous suspensions (i.e., by procedure A, see footnote *a* of Table I), and present evidence points to liquid–liquid phase transfer for the two-phase (procedure B) reactions with thiourea.

In the second method, "substrate–reagent ion-pair reaction," the substrate and reagent become the ion and counterion constituting a salt; the two components then react to form the product. In the examples in this paper we (i) attached a cationic group to the substrate (ROH → **1**), (ii) made the anionic nucleophile the counterion of the new cation, and (iii) allowed the salt to react, usually by heating. These steps also need not

be experimentally distinct; in procedures C1 and C4, generation of the cation automatically gives the correct anion, thereby combining steps i and ii. The C procedures presumably all proceed by this process, but the two-phase systems are potentially mechanistically complex. Some of the betylates, for example, may act as phase transfer agents thereby making it difficult to distinguish between (a) substrate phase transfer (with the actual reaction occurring in the aqueous phase), and (b) "normal" phase transfer of the anion followed by a substrate-reagent ion-pair reaction in the organic phase; micellar and interfacial processes can also further complicate the picture.

Both the phase transfer and ion-pair processes are obviously capable of extension well beyond the betylate reactions given here, and we foresee application of betylate chemistry and of these methods not only in synthesis but in mechanistic and biological studies as well.

Acknowledgment. We thank the National Research Council of Canada for support of this work.

Supplementary Material Available: Preparation and use of betylates (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.
(2) Presented at the CIC/ACS Joint Conference, Montreal, May–June, 1977.
(3) So-called from their formation of betaines **2** on substitution or elimination.
(4) Further experimental details regarding the preparation and use of betylates appear in the microfilm edition. See paragraph at end of paper regarding supplementary material.
(5) In a three-step process, ROH → **3** → **4** (Nu = NMe_2) → **1** (n = 2), taking typically ~1–2 h for 1–100 mmol quantities: J. F. King and S. M. Loosmore, *J. Chem. Soc., Chem. Commun.*, 1011 (1976). The synthesis of methyl [2]betylate perchlorate (**1**, n = 2; R = CH_3; X^- = ClO_4^-) along with 15 other methyl and two ethyl esters of quaternary ammonium sulfonic acids has been described by P. Blumbergs, A. B. Ash, F. A. Daniher, C. L. Stevens, H. O. Michel, B. E. Hackley, Jr., and J. Epstein, *J. Org. Chem.*, **34**, 4065 (1969). These authors demonstrate clearly the utility of these species as water-soluble alkylating agents, but their method lacks the generality as well as the favorable yields and the ease and mildness of our procedures. A recent report also notes the hydrophilic and good leaving group properties of "amsylates" (trimethylammonium benzenesulfonates): C. N. Sukenik and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 6613 (1976).
(6) R. K. Crossland, W. E. Wells, and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **93**, 4217 (1971).
(7) Compound **5** is prepared by reaction of *N*-methyl propanesultam[8] with excess $MeOSO_2F$ at room temperature (J. R. du Manoir, unpublished observation).
(8) A. D. Bliss, W. K. Cline, C. E. Hamilton, and O. J. Sweeting, *J. Org. Chem.*, **28**, 3537 (1963).
(9) These methods are clearly distinguished from current general methods such as phase transfer catalysis or the use of mixed or dipolar aprotic solvent systems in that the latter focus on alteration of the reagent or the medium rather than the substrate.

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Mixed Phenazine–*N*-Methylphenazinium 7,7,8,8-Tetracyano-*p*-quinodimethanide. A Quasi-One-Dimensional "Metal-Like" System with Variable Band Filling

Sir:

In the past few years there has been enhanced activity in the design and synthesis of highly conducting pseudo-one-dimensional (1-D) organic[1,2] and inorganic complexes[2,3] so that the saliant features of such 1-D materials can be understood.[4] To date only a few prototype organic systems have been studied. These are based on 7,7,8,8-tetracyano-*p*-quinodimethanide ($TCNQ^{-}\cdot$) (**2**) salts of heterocyclic open shell sulfur (and/or selenium) (e.g., tetrathiofulvalene (TTF)), and closed shell nitrogen containing (e.g., *N*-methylphenazenium (NMP^+, **1**) cations. The results of such studies and, in particular, the former open shell cation, TTF, has led to significant advances in the understanding of the physics of 1-D organic materials. However, many fundamental questions still persist. Since the charge-transfer organic 1-D complexes studied to date differ in structure and stoichiometry, comparisons between them have to be reported with caution. To alleviate the intrinsic comparative difficulties, we attempted to design an isomorphous series of highly conducting 1-D organic complexes which possess a variable filled conduction band so that the physical properties could be studied as a function of band filling, i.e., Fermi energy.[5] Of the available prototype organic 1-D "metals", $(NMP^+)(TCNQ^{-}\cdot)$[6] was chosen as the model system.[7,8] It seemed reasonable that, if the TCNQ chain provides a driving force for the stabilization of the 1-D structure and if on the average each TCNQ in $(NMP^+)(TCNQ^{-}\cdot)$ is $TCNQ^{1-}$, removal of NMP^+ (and of course the electron associated with its $TCNQ^{-}\cdot$ moiety) would reduce the average charge per TCNQ, i.e., $TCNQ^{z-}$ ($z < 1$). Removal of the cation would destroy the unit cell; however, substitution of the NMP^+ cation with a neutral molecule of comparable size, shape, and polarizability should stabilize the structure.[10] For these reasons the substitution of phenazine, Phen (**3**), for NMP^+ in $(NMP^+)(TCNQ^{-}\cdot)$, (**1**)(**2**), was attempted.

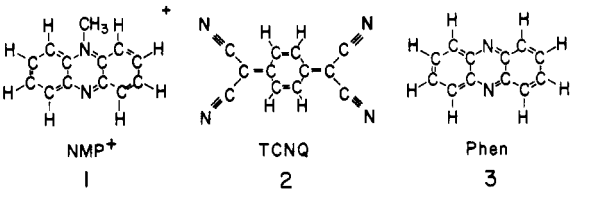
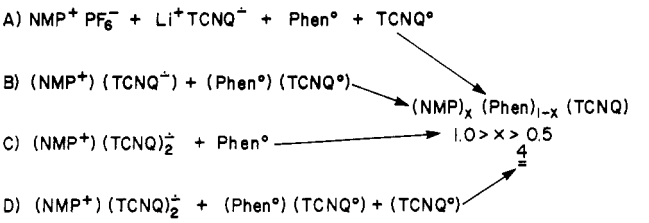


Table I. Unit Cell Parameters for $(NMP)_x(Phen)_{1-x}TCNQ$

	(NMP)(TCNQ)[a]	$(NMP)_{0.74}$-$(Phen)_{0.26}$-TCNQ	$(NMP)_{0.54}$-$(Phen)_{0.46}$-TCNQ
a, Å	3.8682 (4)	3.890 (8)	3.865 (7)
b, Å	7.7807 (8)	7.799 (3)	7.611 (32)
c, Å	15.735 (2)	15.706 (6)	16.329 (51)
α	91.67 (1)	91.75 (6)	93.73 (49)
β	92.67 (1)	92.96 (13)	91.53 (31)
γ	95.38 (1)	95.45 (2)	94.65 (20)
V, Å^3	470.7	473.4	477.4

[a] Reference 19.

Scheme I



Through reactions A, B, C, or D, outlined in Scheme I, complexes of $(NMP^+)_x(Phen)_{1-x}(TCNQ^{-}\cdot)_x(TCNQ^0)_{1-x} \equiv (NMP^+)_x(Phen)_{1-x}(TCNQ)^{x-}$, **4**, stoichiometry with $1 \geq x \gtrsim 0.5$, could be isolated as dark reflecting needle crystals. Visual appearance and crystallographic, elemental composition and differential scanning calorimetry (DSC) measurements, as well as temperature dependence of the conductivity and magnetic susceptibility, indicate that these crystals resemble but are not identical with $(NMP^+)(TCNQ^{-}\cdot)$.[12]

Unit cell determinations were obtained on **4** ($x = 0.24 \pm 0.01$ and 0.46 ± 0.01).[18] The results suggest that **4** ($x = 0.24$

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