



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

Proce- dure <sup>a</sup>	Substrate				Reagent	Conditions, medium (T, °C, time)	Product	% yield <sup>b</sup>
	Betylate	(mmol)	R	X <sup>-</sup>				
A	Me <sub>3</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>2</sub> - SO <sub>2</sub> OR	(11)	1-Butyl	FSO <sub>3</sub> <sup>-</sup>	KSCN	H <sub>2</sub> O (25, 2 h)	RSCN	91
A		(8)	1-Butyl	FSO <sub>3</sub> <sup>-</sup>	Na <sub>2</sub> SO <sub>3</sub>	H <sub>2</sub> O (25, 1 h)	RSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	(80)
C4	HMe <sub>2</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>2</sub> - SO <sub>2</sub> OR	(22)	Neopentyl	I <sup>-</sup>	None	DMF (120-130, 2 h) <sup>c</sup>	RI	68
B	Me <sub>3</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>2</sub> - SO <sub>2</sub> OR	(0.5)	1-Octyl	ClO <sub>4</sub> <sup>-</sup>	KSCN	CHCl <sub>3</sub> :H <sub>2</sub> O (25, 24 h)	RSCN	88
B		(0.5)	1-Octyl	ClO <sub>4</sub> <sup>-</sup>	(NH <sub>2</sub> ) <sub>2</sub> C=S	PhH:H <sub>2</sub> O (25, 21.5 h)	[RSC(NH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	75
C1		(0.25)	1-Octyl	ClO <sub>4</sub> <sup>-</sup>	None	PhCH <sub>3</sub> (110, 1.5 h)	ROClO <sub>3</sub>	92
C3		(0.5)	1-Octyl	I <sup>-</sup>	None	CHCl <sub>3</sub> (61, 0.25 h)	RI	70
B		(0.5)	2-Octyl	FSO <sub>3</sub> <sup>-</sup>	NaN <sub>3</sub> (satd)	CHCl <sub>3</sub> (25, 0.25 h)	RN <sub>3</sub>	85
A		(2.0)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaN <sub>3</sub> (satd)	H <sub>2</sub> O (25, 4 h)	RN <sub>3</sub>	90
A		(1.0)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	KBr	H <sub>2</sub> O (25, 5 h)	RBr	90
A		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	KCN	H <sub>2</sub> O (25, 60 h)	ROSO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CN	90
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaCl	CH <sub>2</sub> Cl <sub>2</sub> :H <sub>2</sub> O (50, 18 h)	RCl	80
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> :H <sub>2</sub> O (50, 16 h)	RONO <sub>2</sub>	65
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	(NH <sub>2</sub> ) <sub>2</sub> C=S	PhH:H <sub>2</sub> O (25, 1 h)	[RSC(NH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> - FSO <sub>3</sub> <sup>-</sup>	75
B		(0.25)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaOAc	CH <sub>2</sub> Cl <sub>2</sub> :H <sub>2</sub> O (25, 2.5 h)	ROSO <sub>2</sub> CH=CH <sub>2</sub>	90
B		(0.25)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaSH	CH <sub>2</sub> Cl <sub>2</sub> :H <sub>2</sub> O (25, 0.25 h)	ROSO <sub>2</sub> CH=CH <sub>2</sub>	60
D		(0.25)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaOEt	EtOH:PhH (25, 3 h)	ROSO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OEt	55
C1		(0.4)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	None	PhCH <sub>3</sub> (110, 0.25 h)	ROSO <sub>2</sub> OR	90
C1		(0.4)	1-Hexadecyl	CH <sub>3</sub> - SO <sub>3</sub> <sup>-</sup>	None	PhCH <sub>3</sub> (110, 1 h)	ROSO <sub>2</sub> CH <sub>3</sub>	74
C1		(0.2)	1-Hexadecyl	ClO <sub>4</sub> <sup>-</sup>	None	PhCH <sub>3</sub> (110, 1.5 h)	ROClO <sub>3</sub>	100
C1		(0.2)	1-Hexadecyl	CF <sub>3</sub> - SO <sub>3</sub> <sup>-</sup>	None	PhCH <sub>3</sub> (110, 2 h)	ROSO <sub>2</sub> CF <sub>3</sub>	67
C3		(0.4)	1-Hexadecyl	SCN <sup>-</sup>	None	CHCl <sub>3</sub> (61, 0.5 h)	RSCN	77
C4	HMe <sub>2</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>2</sub> - SO <sub>2</sub> OR	(0.5)	1-Hexadecyl	Cl <sup>-</sup>	None	PhH (81, 0.25 h)	RCl	100
C4		(0.5)	1-Hexadecyl	I <sup>-</sup>	None	PhH (81, 0.5 h)	RI	92
A	Me <sub>3</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>2</sub> - SO <sub>2</sub> OR	(0.2)	1-Docosyl	FSO <sub>3</sub> <sup>-</sup>	KBr	H <sub>2</sub> O (25, 3.5 h)	RBr	74
B		(0.2)	1-Docosyl	FSO <sub>3</sub> <sup>-</sup>	NaN <sub>3</sub> (satd)	PhH:H <sub>2</sub> O (25, 1 h)	RN <sub>3</sub>	77
B	Me <sub>3</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>3</sub> - SO <sub>2</sub> OR	(1)	1-Butyl	FSO <sub>3</sub> <sup>-</sup>	Imidazole	CHCl <sub>3</sub> :H <sub>2</sub> O (25, 18 h)	1-R-imidazole	84
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaN <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> :H <sub>2</sub> O (25, 24 h)	RN <sub>3</sub>	100
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaSPh	PhH:H <sub>2</sub> O (25, 18 h)	RSPh	85
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaCN	PhH:H <sub>2</sub> O (25, 72 h)	RCN	95
B		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	NaBr	PhH:H <sub>2</sub> O (25, 48 h)	RBr	95
C1		(0.5)	1-Hexadecyl	FSO <sub>3</sub> <sup>-</sup>	None	PhCH <sub>3</sub> (110, 4.5 h)	ROSO <sub>2</sub> OR	85
C2		(0.6)	1-Hexadecyl	Cl <sup>-</sup>	None	PhCH <sub>3</sub> (110, 2 h)	RCl	95
C2		(0.6)	1-Hexadecyl	CN <sup>-</sup>	None	PhCH <sub>3</sub> (110, 2.5 h)	RCN	(60)
C2		(0.5)	1-Hexadecyl	F <sup>-</sup>	None	PhCH <sub>3</sub> (110, 84 h)	RF	(47)
C4	HMe <sub>2</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>3</sub> - SO <sub>2</sub> OR	(0.6)	1-Hexadecyl	Br <sup>-</sup>	None	PhCH <sub>3</sub> (110, 2 h)	RBr	(80)
B	Me <sub>3</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>3</sub> - SO <sub>2</sub> OR	(1.0)	2-Octyl	FSO <sub>3</sub> <sup>-</sup>	NaSPh	PhCH <sub>3</sub> (25, 18 h)	RSPh	60

<sup>a</sup> 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<sub>3</sub><sup>-</sup> salt on Rexyn 201 or 202 resin and evaporation of solvent; C3, by stirring the FSO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> salt in CH<sub>2</sub>Cl<sub>2</sub> with an aqueous solution of excess K<sup>+</sup>Nu<sup>-</sup> for 15-30 min and then separating the organic layer; C4, by adding excess HNu to a CH<sub>2</sub>Cl<sub>2</sub> solution of Me<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SO<sub>2</sub>OR and then evaporating the solvent. <sup>b</sup> 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. <sup>c</sup> Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>O-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.

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**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  $\rightarrow$  **3**  $\rightarrow$  **4** (Nu = NMe<sub>2</sub>)  $\rightarrow$  **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]betylperchlorate (**1**,  $n = 2$ ; R = CH<sub>3</sub>; X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>) along with 15 other methyl and two ethyl esters of quaternary ammonium sulfonic acids has been described by P. Blumberg, A. B. Ash, F. A. Danilher, 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<sup>8</sup> with excess MeOSO<sub>2</sub>F 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:

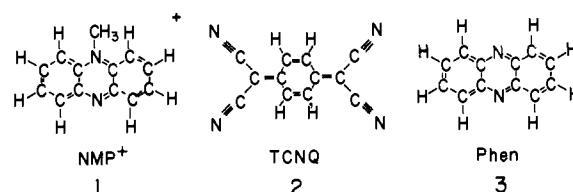
In the past few years there has been enhanced activity in the design and synthesis of highly conducting pseudo-one-dimensional (1-D) organic<sup>1,2</sup> and inorganic complexes<sup>2,3</sup> so that the salient features of such 1-D materials can be understood.<sup>4</sup> To date only a few prototype organic systems have been studied. These are based on 7,7,8,8-tetracyano-*p*-quinodimethanide (TCNQ<sup>-</sup>) (**2**) salts of heterocyclic open shell sulfur

**Table I.** Unit Cell Parameters for (NMP)<sub>x</sub>(Phen)<sub>1-x</sub>TCNQ

	(NMP) (TCNQ) <sup>a</sup>	(NMP) <sub>0.74</sub> <sup>-</sup> (Phen) <sub>0.26</sub> <sup>-</sup> TCNQ	(NMP) <sub>0.54</sub> <sup>-</sup> (Phen) <sub>0.46</sub> <sup>-</sup> TCNQ
<i>a</i> , Å	3.8682 (4)	3.890 (8)	3.865 (7)
<i>b</i> , Å	7.7807 (8)	7.799 (3)	7.611 (32)
<i>c</i> , Å	15.735 (2)	15.706 (6)	16.329 (51)
$\alpha$	91.67 (1)	91.75 (6)	93.73 (49)
$\beta$	92.67 (1)	92.96 (13)	91.53 (31)
$\gamma$	95.38 (1)	95.45 (2)	94.65 (20)
<i>V</i> , Å <sup>3</sup>	470.7	473.4	477.4

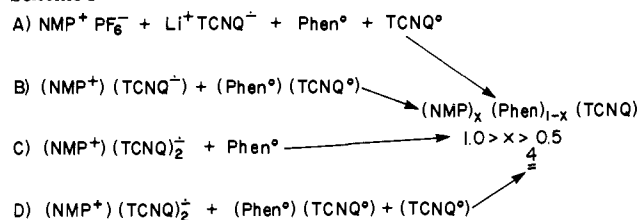
<sup>a</sup> Reference 19.

(and/or selenium) (e.g., tetrathiofulvalene (TTF)), and closed shell nitrogen containing (e.g., *N*-methylphenazinium (NMP<sup>+</sup>, **1**) cations. The results of such studies and, in par-



ticular, 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.<sup>5</sup> Of the available prototype organic 1-D "metals", (NMP<sup>+</sup>)(TCNQ<sup>-</sup>)<sup>6</sup> was chosen as the model system.<sup>7,8</sup> 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<sup>+</sup>)(TCNQ<sup>-</sup>) is TCNQ<sup>1-</sup>, removal of NMP<sup>+</sup> (and of course the electron associated with its TCNQ<sup>-</sup> moiety) would reduce the average charge per TCNQ, i.e., TCNQ<sup>z-</sup> ( $z < 1$ ). Removal of the cation would destroy the unit cell; however, substitution of the NMP<sup>+</sup> cation with a neutral molecule of comparable size, shape, and polarizability should stabilize the structure.<sup>10</sup> For these reasons the substitution of phenazine, Phen (**3**), for NMP<sup>+</sup> in (NMP<sup>+</sup>)(TCNQ<sup>-</sup>), (**1**)(**2**), was attempted.

### Scheme I



Through reactions A, B, C, or D, outlined in Scheme I, complexes of (NMP<sup>+</sup>)<sub>x</sub>(Phen)<sub>1-x</sub>(TCNQ<sup>-</sup>)<sub>x</sub>(TCNQ<sup>0</sup>)<sub>1-x</sub>  $\equiv$  (NMP<sup>+</sup>)<sub>x</sub>(Phen)<sub>1-x</sub>(TCNQ)<sup>x-</sup>, **4**, stoichiometry with  $1 \geq x \geq 0.5$ , 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<sup>+</sup>)(TCNQ<sup>-</sup>).<sup>12</sup>

Unit cell determinations were obtained on **4** ( $x = 0.24 \pm 0.01$  and  $0.46 \pm 0.01$ ).<sup>18</sup> The results suggest that **4** ( $x = 0.24$