

# Charge-Transfer Interaction and Transition between Donor and Acceptor Components Fixed in a Rigid Spatial Arrangement. Generalization and Molecular Design

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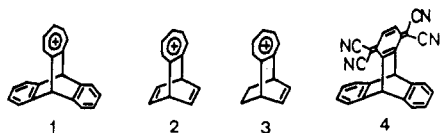
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Received October 25, 1982

Charge-transfer interaction (CTI) and transition (CTT) between donor and acceptor components fixed in the frameworks of  $C_{2v}$  and  $C_s$  point groups are discussed. The  $C_{2v}$  and  $C_s$  systems being considered are classified into modes 1-4 and 5-8, respectively, simply by the symmetry properties of the components involved. The features of the systems enable us to examine the effects of the geometry on the CT phenomena in the intramolecular remote CT complexes, especially the selection rules. Molecular design of the CT complexes is attained by using the typical donor and acceptor components. Our arguments on CTT for a symmetry-forbidden CTI contribute to the elimination of a misunderstanding among some that the appearance of a CTT is an indication of a significant CTI between the donor and acceptor in the ground state. Furthermore, such transitions are expected to polarize perpendicular to the donor-acceptor axis.

Mulliken's valence bond treatment of weak intermolecular complexes between electron donors and acceptors provided a main stimulus to the extensive developments in the rich and varied field of chemistry and physics related to intermolecular charge-transfer (CT) interaction and transition (CT phenomena).<sup>2-6</sup>

The CT concept has also been applied to a wide range of problems in the intramolecular CT complexes. Since the first synthesis of triptycene by Bartlett and co-workers<sup>7</sup> in 1942, transannular electronic interaction between the remote (nonconjugated) benzene rings has been of particular interest.<sup>8</sup> In order to investigate such an interaction, it is important to select the pertinent model system and the proper method of measurements which should be sufficiently sensitive to detect the interaction. To this end we have designed an intramolecular CT complex, viz., 9,10-dihydro-9,10-(*o*-tropylio)anthracene tetrafluoroborate (1), in which intramolecular CT transition can be observed

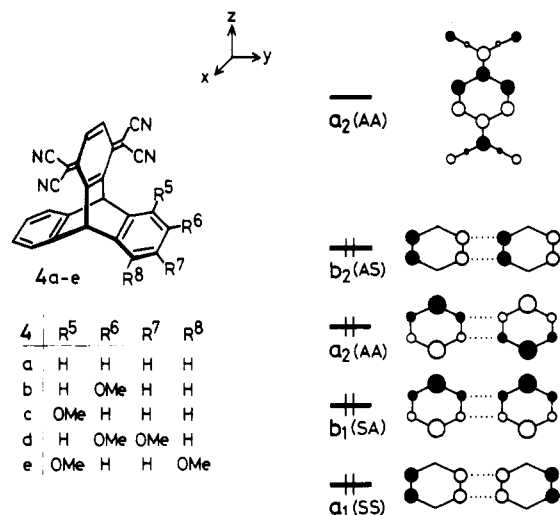


- (1) (a) Osaka University. (b) Kobe University. (c) Gifu University.  
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 (7) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* 1942, 64, 2649.  
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as a separate band at considerably longer wavelength region than those of the component chromophors. In fact, the electronic spectrum of 1 exhibited a clear CT transition between the benzene and the tropylium rings in the long-wavelength region (300-450 nm) as a broad band.<sup>9</sup> Olefins should conceivably be able to replace the aromatic hydrocarbon moiety as the donor for a more fundamental probe. In this context, the tropylium analogues of barrelene (2)<sup>10</sup> and of bicyclo[2.2.2]octa-2,5-diene (3)<sup>11</sup> were also prepared and found to be simpler models for such CT complexes.

In the intramolecular remote CT complexes, the donor and acceptor components are rigidly fixed to be nonparallel with no direct conjugation between them. This characteristic of the complexes allows us to build up the pertinent model system and to simplify and amplify the essential point in the problems. Although the tropylium ion was found to be a good electron acceptor, the doubly degenerate LUMOs of the ion may complicate the situation being considered. Since tetracyanoquinodimethane (TCNQ), known as a strong electron acceptor, has a low-lying single LUMO, the triptycene-type compound in which a benzene ring is replaced by a TCNQ ring seems to be an attractive model compound for the analysis of the intramolecular CT phenomena. More recently we synthesized 1,4-dihydro-1,4-bis(dicyanomethylene)triptycene (4a)<sup>12a</sup> and a series of TCNQ triptycenes (4b-e).<sup>12</sup> 4a showed the distinct CT transition in its electronic spectrum. In 4a, which belongs to the  $C_{2v}$  point group, the HOMOs are four high-lying occupied molecular orbitals mainly localized on the electron-donating benzene rings. The LUMO is considered to be localized on the electron-accepting TCNQ moiety. Thus, in 4a, the lowest energy CT transition ( $b_2 \rightarrow a_2$ ) is symmetry allowed while the CT interaction between the corresponding HOMO( $b_2$ )-

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 (12) (a) Yamamura, K.; Nakazawa, T.; Murata, I. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 543. (b) Inagaki, S.; Yamamura, K.; Nakasuji, K.; Nakazawa, T.; Murata, I. *J. Am. Chem. Soc.* 1981, 103, 2093. See also: Yamamura, K.; Nakasuji, K.; Murata, I.; Inagaki, S. *J. Chem. Soc., Chem. Commun.* 1982, 396. (c) Murata, I. *Pure Appl. Chem.* 1983, 55, 323.

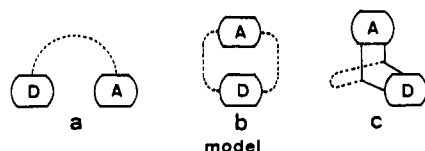


LUMO( $a_2$ ) is symmetry forbidden. Furthermore, the charge transfer in the ground state occurs only from the second HOMO ( $a_2$ ) to the LUMO ( $a_2$ ). Such a phenomenon—CT transition for symmetry-forbidden CT interaction—was further supported by the unequivocal experimental evidence by using the substituent effects on the CT band shifts. Thus in accord with the feature of the AO coefficients in the HOMO( $b_2$ ), the red shifts are observed only when the electron-donating methoxy groups are substituted at the 6- (**4b**) and 6,7-positions (**4d**) on a benzene ring. These results provide decisive evidence for the fact that the orbitals involved in the ground state CT interaction need not be the same as those involved in the CT transition.

Now, taking into account the above-mentioned result, we describe the generalization of the relationship between the remote CT phenomena and the symmetry properties of the donor and acceptor components. The molecular design of the possible intramolecular remote CT complexes and some predictions regarding hitherto unknown systems will also be described in some detail.

### Generalization of the Properties of Charge-Transfer Interaction and Transition in Intramolecular Remote Charge Transfer

Certain molecules contain both effective donor and acceptor components without direct conjugation. The intramolecular remote CT phenomena might occur if the molecule exists in a conformation so as to overlap the orbitals of the components and satisfy the symmetry requirements between them. This type of phenomena is contrasted with the one occurring within a directly conjugated intramolecular system such as in *p*-nitroaniline and can provide more fundamental information for intermolecular CT phenomena. The remote complexes are classified into three main types: a–c. Model a consists of



the donor and acceptor components connected with an unconjugated chain, whereas models b and c include such components fixed in a parallel and nonparallel rigid spatial arrangement, respectively. Although model c suffers at least one disadvantage in that the extent of the overlap between the components will be considerably diminished, it possesses the advantage that the geometrical arrange-

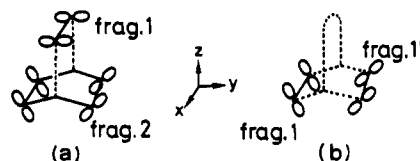


Figure 1. Illustration of the fragments in (a)  $C_{2v}$  and (b)  $C_s$  systems.

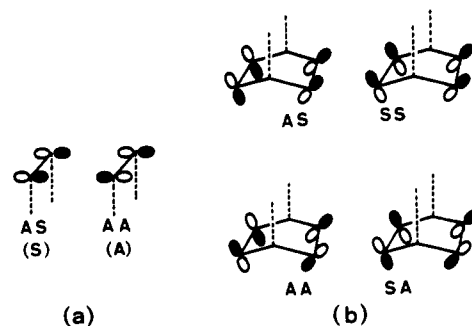


Figure 2. Symmetry properties of (a) fragment 1 (or 1') and (b) fragment 2.

ment of the components might be adjusted unequivocally and rigidly without adding serious strain to the components.

The present discussion is concerned with the selection rules of CT interaction (CTI) and CT transition (CTT) in model c, which belongs to the  $C_{2v}$  or  $C_s$  point group, as do 1 or 3, respectively. The reasons why we choose the systems containing both a relatively high-lying HOMO of the donor component and a relatively low-lying LUMO of the acceptor are as follows. First, in such systems the CTT might appear as a separate band at considerably longer wavelengths than the local excitations within the components, so that clear-cut experimental results are expected.<sup>13</sup> For our present purpose the qualitative arguments are enough to discuss the CTT involved. Second, though both through-space and through-bond interactions between the components usually must be invoked to account properly for possible CTI and CTT in the system, the simple symmetry arguments in the case of the system stated above, based only on through-space interactions, might provide proper information in a very simple and straightforward manner.

The  $C_{2v}$  system is divided into two fragments, 1 and 2, as illustrated in Figure 1a. The symmetry properties of the fragment orbitals are classified with respect to the reflection in the  $xz$  and  $yz$  planes, in order. In fragment 1 there are two symmetry properties, AS and AA (Figure 2a). In fragment 2 there are two sets of symmetry properties (Figure 2b). One of them, SS and AS, is in-phase and out-of-phase combinations of the orbitals which are symmetric with respect to the  $yz$  plane. The other set, SA and AA, is similar combinations of the orbitals which are antisymmetric with respect to the  $yz$  plane.

One may connect each of the symmetry properties of the fragments in four possible modes, 1–4, as indicated in the first to third columns of Table Ia. The selection rule for CTI is derived simply from the products of symmetry properties in each fragment. CTI is allowed only in the case of product SS. The selection rule for CTT is derived from both the products and the symmetry properties of each component in the three Cartesian coordinate axes of

(13) In other words, the locally excited configurations are mixed into the electron-transferred configurations to only a small extent in the first excited state. Theoretical analysis is facilitated by the one-configuration predominance.

Table I. Symmetry Properties and Selection Rules of Possible Modes in the (a)  $C_{2v}$  and (b)  $C_s$  Systems

(a) $C_{2v}$ System						
mode	symmetry properties			selection rules <sup>a</sup>		
	frag 1	frag 2	product	CTI	CTT	
1	AS	AS	SS	a	a (z)	
	AS	SS	AS	f	a (y)	
2	AS	AA	SA	f	a (x)	
	AS	SA	AA	f	f	
3	AA	AS	SA	f	a (x)	
	AA	SS	AA	f	f	
4	AA	AA	SS	a	a (z)	
	AA	SA	AS	f	a (y)	

(b) $C_s$ System						
mode	symmetry properties			selection rules <sup>a</sup>		
	frag 1	frag 1'	product	CTI	CTT	
5	S	S	S	a	a (y,z)	
6	S	A	A	f	a (x)	
7	A	S	A	f	a (x)	
8	A	A	S	a	a (y,z)	

<sup>a</sup> a = allowed and f = forbidden.

Table II. Typical Examples of (a) Donor and (b) Acceptor Components

(a)	
S	
A	
S,A	
(b)	
S	
A	
S,A	

the dipole moment vector.<sup>14</sup> Thus the products SA, AS, and SS correspond to symmetry-allowed transitions with polarization along the x, y, and z axis, respectively. Product AA corresponds to a symmetry-forbidden transition. The selection rules for the  $C_{2v}$  system are summarized in the last two columns of Table Ia.

There are four possible modes, 5–8, in the  $C_s$  system (Figures 1b and 2a). Table Ib presents the generalizations of the properties of each mode. The product S corresponds to symmetry-allowed CTI and CTT whereas the product A corresponds to forbidden CTI and allowed CTT. These

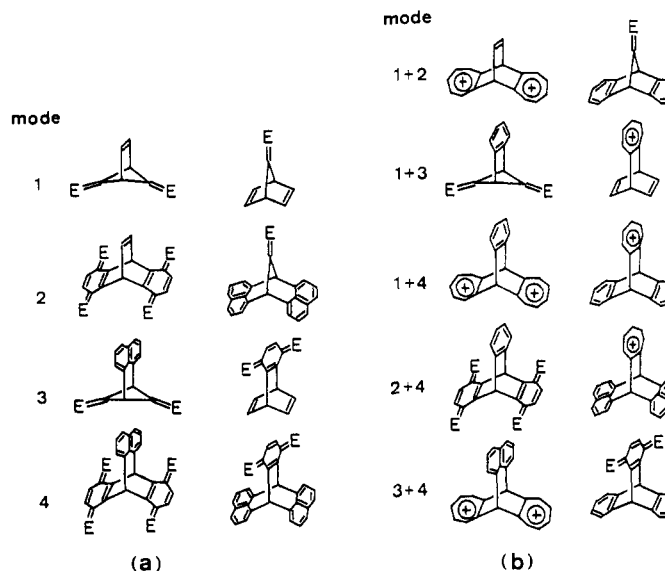


Figure 3. Examples of molecular design of the remote CT complexes in the  $C_{2v}$  system with (a) nondegenerate and (b) degenerate components. E = C(CN)<sub>2</sub>.

Table III

compd	mode	compd	mode
1	1 + 4	3	5 + 6
2	1 + 3	5	5 + 8
4	3 + 4	6	5 + 6

results can be confirmed by explicit group theoretical treatments.

### Molecular Design of Intramolecular Remote Charge-Transfer Complexes

If each fragment is replaced by pertinent, actual donor or acceptor components, the molecular design is attained. Table II lists typical examples of donor and acceptor components which are classified by the symmetry properties of the HOMO of donors and the LUMO of acceptors, S and/or A, with respect to the reflection in the yz plane. Since they are embodied in a simple form, the appropriate modification or introduction of substituents would be required to design better model systems. Consideration of only the symmetry property of the components with respect to the yz plane can simply lead us to the desired molecular design. Figure 3a exemplifies molecules of modes 1–4 by the replacement of each fragment with the components designated in parentheses in Table II. There are two types of molecules in each mode, since each fragment can be displaced by either donor or acceptor components to build up the actual structure.

The properties of the systems with doubly degenerate orbitals on the components are represented by the combination of two different modes in Table Ia. There are five degenerate modes as indicated in Figure 3b. For example, the combination of the modes 1 and 2 (denoted by mode 1 + 2) gives rise to four groups of different symmetry properties. The mode 1 + 4 contains all eight symmetry properties in Table Ia.

Figure 4a illustrates actual examples for the  $C_s$  system with nondegenerate components. The degenerate modes are indicated in Figure 4b. The mode 5 + 8 is expressed in terms of all four properties in Table Ib. In Figure 4 for the  $C_s$  system, each mode contains one kind of molecule.

### Discussion

In the intermolecular CT complexes the relative orientation of the donor and acceptor components is initially

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Table IV. Correlation between the Properties of 2 (Mode 1 + 3) and Calculated and Experimental Data

frag 1	frag 2	CTI <sup>a</sup>	CTT <sup>a</sup>	calcd (CNDO/S)		obsd ΔE(MCD), eV
				orbital	ΔE, eV	
AA	AS	f	a(x)	32(AA) ← 31(AS)	3.21	3.23
AA	SS	f	f	32(AA) ← 30(SS)	3.49 (f)	
AS	AS	a	a(z)	33(AS) ← 31(AS)	3.52	
AS	SS	f	a(y)	33(AS) ← 30(SS)	3.65	

<sup>a</sup> a = allowed and f = forbidden.

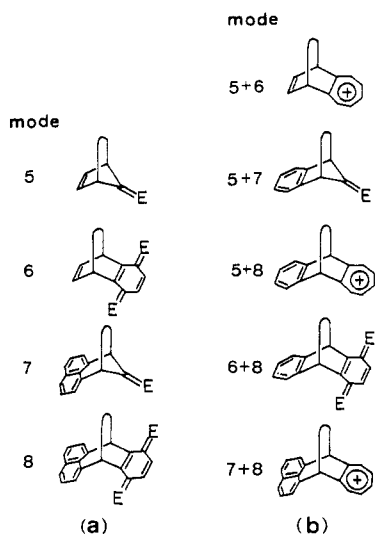


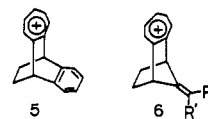
Figure 4. Examples of molecular design of the remote CT complexes in the  $C_{2v}$  system with (a) nondegenerate and (b) degenerate components. E = C(CN)<sub>2</sub>.

determined by CT forces and/or other binding forces.<sup>15</sup> In contrast, the intramolecular remote CT complexes contain two fundamental features: (1) it is possible to modify both the relative orientation and the distance between the components by molecular architecture; (2) it is not necessary to consider the dissociation of the complexes into the components. Feature 1 enables us to examine the effects of the geometry on the CT phenomena in the CT complexes, especially on the selection rules. Thus, Table I shows the allowedness (a) and forbiddenness (f) in each mode. In the  $C_{2v}$  system, each of modes 1–4 contains two types of selection rules for the CT phenomena because each set of symmetry properties in fragment 2 is composed of two symmetry properties (Figure 2b). Thus a total of eight different combinations of symmetry properties of the fragments are obtained. Among them, only the case in which both CTI and CTT are allowed is found in one of the combinations of mode 1 or 4. In the remaining six cases, CTI is symmetry forbidden. Note that the allowed CTT in mode 2 or 3 is restricted only to the transition for symmetry-forbidden CTI. In the  $C_s$  system, the transitions in modes 5 and 8 correspond to CTT for symmetry-allowed CTI (CTT for CTI), and the transitions in modes 6 and 7 correspond to CTT for symmetry-forbidden CTI (CTT for no CTI). These facts unambiguously indicate that the analysis of CTI and CTT has to be done independently.

(15) At present chemical and physical studies of such CT complexes have already been performed extensively and have opened up the development of the chemistry and physics of so-called organic metals in which charge transfer is one of dominant roles for the essential properties. Some of the reviews are as follows: (a) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 519. (b) Torrance, J. B. *Acc. Chem. Res.* 1979, 12, 79. (c) Wheland, R. C.; Gilson, J. L. *J. Am. Chem. Soc.* 1976, 98, 3916. Wheland, R. C. *Ibid.* 1976, 98, 3926. (d) Keller, H. J., Ed. "Chemistry and Physics of One-Dimensional Metals"; Plenum Press: New York, 1977. (e) Alcácer, L., Ed. "The Physics and Chemistry of Low Dimensional Solids"; Reidel: Dordrecht, Holland, 1980.

Our arguments of CTT for no CTI contribute to the elimination of a misunderstanding among some that a CTT is an indication of a significant CTI between donor and acceptor in the ground state. Dewar correctly pointed out in 1965 that "the appearance of a CTT provides no evidence that CT plays a dominant, or even a significant, role in the binding".<sup>16</sup> Unfortunately, there has never been such convincing experimental evidence as the substituent effect on the CT band of 4.<sup>12</sup> More compelling information is expected from the experimental determination of the direction of the transition moments. CTT in most of the intermolecular CT complexes reported so far is polarized along the donor–acceptor axis. Actually, in our intramolecular case, modes 1 and 4 in the  $C_{2v}$  system contain such a transition polarized along the donor–acceptor axis. All these transitions, however, correspond to CTT for CTI. Mulliken,<sup>17</sup> 17 years after his first paper<sup>2</sup> on CT complexes, noted the possibility that the CTT of a benzene–halogen complex is polarized perpendicular to the donor–acceptor axis. Such a transition may be characterized with CTT for no CTI, and it has never before, to our knowledge, been reported for intramolecular CT complexes. A series of dicyanomethylenetriptycenes (4) is the first in which such CTT for no CTI has been successfully observed, as a well-separated band in the longest wavelength region, together with experimental support by the substituent effect. Further verification of CTT for no CTI by the polarized absorption spectrum of a pertinent model compound is now in progress. The intensity of CTT for no CTI can be borrowed from local excitation in the donor or acceptor components of the complexes, though the borrowing is, in principle, not necessary.<sup>17,18</sup>

Table III shows the correlation between the CT complexes synthesized in our laboratories and their corresponding modes. All of them (1–6) belong to the degenerate modes. Although the degenerate components may



complicate the situation, they exhibit the characteristic advantage that we can utilize the additional information obtained from the substituent effect, as observed in 4.<sup>12</sup> With molecule 2 as an example, one of the procedures for the analysis of the properties of these molecules is explained here in more detail. The symmetry properties of fragment 1 in 2 (degenerate tropylium LUMOs) with respect to the reflection in the  $yz$  plane are S and A, and the symmetry property of fragment 2 with respect to the  $yz$  plane is S. Molecule 2 therefore belongs to mode 1 + 3, which involves CT phenomena of four different symmetry properties (Table Ia). The results are summarized in Table IV together with the data of the theoretical calculations

(16) Dewar, M. J. S.; Thompson, C. C., Jr. *Tetrahedron* 1966, *Suppl.* 7, 97.

(17) Reference 5, Chapter 11.

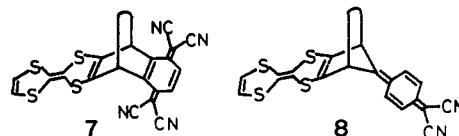
(18) Reference 5, Chapter 13.

and of the magnetic circular dichroism (MCD) measurements.<sup>19</sup>

### Perspective

Powerful donor and acceptor components incorporated in a rigid framework are expected to lead to unprecedented electronic systems with interesting properties. For the forbidden CTI, the ground-state wave function,  $\Psi_G$ , is approximated to be the ground-state configuration,  $\Phi$  (DA), of the closed-shell structure or the electron-transferred configuration,  $\Phi(D^+A^-)$ , of the open-shell structure. In the former closed-shell structure, i.e.,  $\Psi_G \approx \Phi(DA)$ , almost one electron transfers in the first excited state, i.e.,  $\Psi_E \approx \Phi(D^+A^-)$ . Interesting photochemical behavior is expected from the distinct charge separation. In the latter open-shell structure, strong donor-acceptor pairs may give

rise to intramolecular radical ion pairs in the ground states. Such electronic situations can be seen in the hypothetical molecule 7 which belongs to mode 6. On the other hand,



the unknown molecule 8 is also of interest. In contrast to 7, CTI is allowed in 8 which belongs to mode 5. Therefore, the molecule is expected to contain a considerable contribution of the ionic structure in the closed-shell ground state in spite of a diminished amount of the orbital overlap between the components. It would obviously be of great interest to see if these predictions are realized experimentally.

(19) Tajiri, A.; Hatano, M.; Nakasuji, K.; Nakazawa, T.; Murata, I. *Ber. Bunsenges. Phys. Chem.* 1982, 86, 228.

Registry No. 1·BF<sub>4</sub><sup>-</sup>, 63166-75-6; 2·BF<sub>4</sub><sup>-</sup>, 76466-39-2; 3·BF<sub>4</sub><sup>-</sup>, 73101-19-6; 4a, 73524-84-2; 4b, 73524-85-3; 4c, 77493-09-5; 4d, 77478-11-6; 4e, 77478-12-7.

## Lithiation of $\alpha$ -Nitrosaminoalkyl Ethers. Synthetic Equivalents of $\alpha$ -Primary Amino Carbanions<sup>1</sup>

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Received October 4, 1982

Successful experiments directed toward the C-1 alkylation and hydroxyalkylation of primary amines are reported. Primary amines are converted into their *N*-nitroso-*N*-(1-methoxyethyl) derivatives, which are subsequently lithiated and condensed with various electrophiles, denitrosated, and hydrolyzed to produce the desired compounds in good to excellent yields.

Metalation of nitrosamines is a well-established method of considerable synthetic value for preparing masked  $\alpha$ -secondary amino carbanions.<sup>2</sup> The metalated nitrosamine can undergo reaction with a great variety of electrophiles at the  $\alpha$ -carbon, and the secondary amine can be regenerated by using standard procedures.<sup>2,3</sup>

On the other hand, umpolung reactivity for primary amines is a more complicated process. The best known method involves preparation of the corresponding isocyanide. This derivative is lithiated to react with electrophiles, followed by hydrolytic demasking to the primary amine.<sup>4</sup> Another method, with more limited applicability, requires oxidation of the amine to the nitro group<sup>5</sup> as the initial step.

One pathway by which the reactivity of a primary amine could be reversed is to convert it to a chemical species similar to a secondary amine which can then be nitrosated. The nitrosamine would then undergo electrophilic attack at the  $\alpha$ -carbon, and, finally, a demasking step would regenerate the primary amine (Scheme I).  $\alpha$ -Nitrosaminoalkyl ethers are the type of compound meeting the

Scheme I

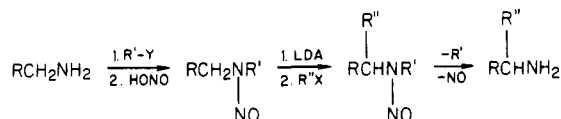


Table I. Reaction of Lithio- $\alpha$ -nitrosaminoalkyl Ethers with Electrophiles

nitrosamine	electrophile	product (yield, %)	primary amine (yield, %)
1	MeI	3 (80%)	EtNH <sub>2</sub> ·HCl (80%)
3	MeI	4 (52%)	(Me) <sub>2</sub> CHNH <sub>2</sub> ·HCl (84%)
1	MeCHO	5a,b (77%)	MeCHOCH <sub>2</sub> NH <sub>2</sub> ·HCl (92%)
1	(Me) <sub>2</sub> CO	6 (78%)	(Me) <sub>2</sub> COHCH <sub>2</sub> NH <sub>2</sub> ·HCl (90%)
1	BzBr	7 (86%)	Ph(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> (56%)
1	EtI	8 (55%)	Me(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> ·HCl (93%)
1	<i>n</i> -PrI	9 (43%)	Me(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> ·HCl (87%)

characteristics described above. These compounds, as well as the  $\alpha$ -acetoxy analogues, have been widely used as model

<sup>†</sup> Research sponsored by the National Cancer Institute, DHHS, under contract No. NO1-CO-23909 with Litton Bionetics, Inc. The contents of this publication do not necessarily reflect the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government.

(1) Presented in part at the 16th Annual Middle Atlantic Regional Meeting of the American Chemical Society, Newark, DE, April 21-23, 1982; Abstract No. ORGN 250.