

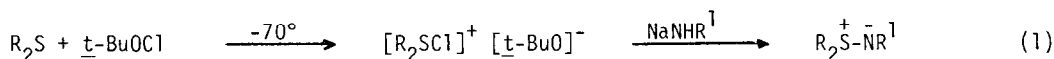
A NONAZIDE SOURCE OF CYANONITRENE AND ITS INTERCEPTION BY TERTIARY AMINES

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Summary: Cyanonitrene is formed from sodium cyanamide and *t*-butyl hypochlorite in methanol by an  $\alpha$ -elimination at or above 0° to +10°, but not at lower temperatures. The nitrene has been trapped by tertiary amines to yield aminimides in fair to good yields. The formation of cyanonitrene has been shown by ESR, dimerization to dicyanodiazene, and reaction with DMSO to yield the sulfoximine.

In 1972 we showed that the intermediates formed at low temperatures (<-30°) from *t*-butyl hypochlorite (BHC) and thioethers react readily with sodium salts of sulfonamides, carboxamides and cyanamide to yield sulfilimines in 25-80% yields (Eq. 1).<sup>1</sup> With appropriate



(R = Ph, Me; R<sup>1</sup> = CN, PhSO<sub>2</sub>, PhCO, MeCO, ClCH<sub>2</sub>CO, Cl<sub>2</sub>CHCO)

starting materials, an iminophosphorane, Ph<sub>3</sub>P<sup>+</sup>-NCN<sup>-</sup> (from triphenyl phosphine, BHC and sodium hydrogen cyanamide), and a carbosulfurane, Me<sub>2</sub>S<sup>+</sup>-C(CN)<sub>2</sub><sup>-</sup> (from Me<sub>2</sub>S, BHC and the sodium salt of malonitrile), are also obtained in up to 80% yields. These preliminary results suggested that we had in hand a general, simple, one pot procedure for the preparation of many types of ylids from readily available and inexpensive starting materials. In particular, we were interested in the preparation of aminimides,  $\Rightarrow \underline{N}^+ \bar{N}^-$ , by direct N-N coupling.

However, when we attempted to prepare N-arylsulfonylaminimides, R<sub>3</sub>N<sup>+</sup>-NSO<sub>2</sub>Ar, from tertiary amines, BHC, and sodium salts of arylsulfonamides between -50° and room temperature, the only products isolated were the starting sulfonamides and their N-sodio-N-chloroderivatives (chloramines). The low temperature reaction (<-20°) of trimethylamine (and other tertiary amines), BHC, and sodium hydrogen cyanamide yielded no isolable reaction products (starting materials recovered) but, in contrast to the arylsulfonamide experiments, when the reaction mixture was allowed to warm to room temperature precipitation of sodium chloride occurred abruptly about 0° to +10° and a good yield (60-75%) of the aminimide, R<sub>3</sub>N<sup>+</sup>-NCN<sup>-</sup>, was obtained.

The successful synthesis of (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>-NCN<sup>-</sup> can be rationalized by assuming that cyanonitrene is formed from N-sodio-N-chlorocyanamide, Na<sup>+</sup>-N<sup>-</sup>-CN, by an  $\alpha$ -elimination reaction between 0° to 10° but not at the low temperatures originally employed. The elimination

is immediately followed by interception of the nitrene by certain tertiary amines, described below, to form a N-N bond between the electrophilic nitrene and the nucleophilic tertiary amine.

Evidence to support the conclusion of direct N-N bonding via a nitrene or nitrenoid species was obtained both experimentally and from information already available in the literature:

1. DMSO and tertiary amines are known to react with nitrenes, but not with chloramines, to yield sulfoximines<sup>2</sup> and aminimides,<sup>3</sup> respectively. When we react BHC with sodium hydrogen cyanamide in methanol at low temperatures ( $< -50^\circ$ ) an immediate exotherm is observed. If DMSO or a tertiary amine is added while maintaining the low temperature, no further reaction appears to occur and neither sulfoximine (<1%) nor aminimide is obtained. If the reaction system is allowed to warm to room temperature, however, sodium chloride precipitates suddenly between  $0^\circ$  to  $10^\circ$  and fair yields of sulfoximine (35%) and aminimide (60-75%), respectively, are obtained.

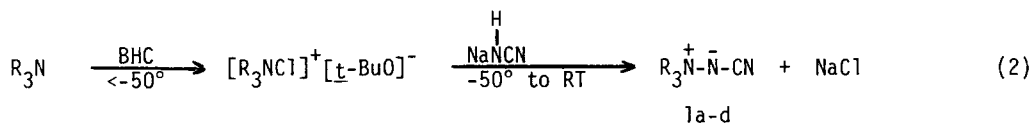
2. That a reactive intermediate is present in the low temperature reaction system of BHC with sodium hydrogen cyanamide is shown by the immediate formation of S,S-dimethyl-N-cyanosulfilimine (60-75%) if dimethyl sulfide is added even though the reaction temperature is not allowed to rise above  $-50^\circ$ . The intermediate at low temperature is most probably N-sodio-N-chlorocyanamide,  $\text{Na}-\overset{\text{Cl}}{\text{N}}-\text{CN}$ , the putative nitrene precursor.

3. If the low temperature BHC/sodium hydrogen cyanamide/methanol reaction system is allowed to warm to room temperature without adding any intercepting nucleophiles, sodium chloride precipitates between  $0^\circ$  to  $+10^\circ$  and the solution becomes deeply orange-colored. Filtration and vacuum evaporation of the filtrate yields an orange, unstable residue which exploded on two separate occasions. The orange solid was identified as dicyanodiazene,  $\text{N}=\text{C}-\text{N}=\text{N}-\text{C}\equiv\text{N}$ , the dimerization product of cyanonitrene. It has the following characteristics: mp  $45-50^\circ$  (dec.); IR, 2200 ( $\text{C}\equiv\text{N}$ ),  $1650\text{ cm}^{-1}$  ( $\text{N}=\text{N}$ );  $^1\text{H}$  NMR, no signal (benzene- $d_6$ );  $^{13}\text{C}$  NMR, 114 ppm (methanol- $d_4$  and benzene- $d_6$ ); mass spectrum, m/e 40 (base peak). Dicyanodiazene had been prepared earlier from cyanogen azide via cyanonitrene,<sup>4</sup> but the compound has received only limited study since.<sup>5</sup>

4. While the present work was in progress, Kemp, Ellis and Closier<sup>6</sup> reported that the reaction of cyanamide with iodosobenzene diacetate produced a nitrene or nitrene-like reaction product that could be trapped by DMSO, dimethyl sulfide, dicyclopentadiene and penicillanic acid.

5. Finally, the BHC/ $\overset{\text{H}}{\text{N}}-\text{CN}$ -methanol system was monitored by EPR from  $-50^\circ$  to room temperature.<sup>7</sup> No signal was observed until a cavity temperature of ca.  $+5^\circ$  was reached, at which point a signal attributable to triplet cyanonitrene was obtained ( $g = 2.0050$ ).<sup>7</sup> Cyanonitrene is presumably generated initially in the singlet state but, in the absence of suitable interceptors, undergoes intersystem crossing to the triplet whose EPR spectrum we are presumably observing.<sup>8</sup>

The formation of aminimides by direct N-N bonding of tertiary amines with cyanonitrene was studied in four cases shown in Equation 2.<sup>9</sup>



[R<sub>3</sub>N derived respectively from quinuclidine (1a),<sup>10</sup> N-methylmorpholine (1b),<sup>11</sup> trimethylamine (1c),<sup>12</sup> and triethylamine (1d).<sup>13</sup>].

#### Typical Preparative Procedure for Aminimides

To a cold (<-50°) stirred solution of t-butyl hypochlorite (1 g, 9 mmol) in methanol (30 ml) a methanol solution (30 ml) of tertiary amine (10 mmol) was added. After 1 hr, a methanol solution (30 ml) of previously prepared sodium cyanamide (10 mmol) (see below) was slowly added while maintaining the reaction temperature below -50° until the addition was complete. The cooling bath was removed and stirring was continued for a minimum of 3 hrs after the reaction mixture reached room temperature. The methanol was evaporated, methylene chloride (250-300 ml) was added to the residue, and the mixture was stirred for 2-4 hrs. The mixture was filtered and the solvent was evaporated from the filtrate. The residue of crude aminimide was obtained in 60-100% yield. One recrystallization of the quinuclidine aminimide yielded the analytically pure sample.<sup>10</sup> The aminimide from N-methylmorpholine required repeated recrystallization from acetone.<sup>11</sup>

Sodium cyanamide was freshly prepared for each reaction from freshly cut sodium (0.23 g, 10 mmol), methanol (30 ml) and cyanamide (0.42 g, 10 mmol). This solution was stirred for 2 hrs at room temperature before use.

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7. Varian EPR V 4500-10A, equipped with Varian V 4540 temperature controller. Original spectra can be found in Ph.D. thesis of M.G.K.H., Temple University, 1981.
8. Suitable control experiments were run. Of particular significance, control experiments

in which sodium hydrogen cyanamide was omitted from the reaction system produced no signal; an absolutely flat line was obtained from  $-50^{\circ}$  to room temperature.

9. All products were characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and/or mass spectra, and elemental analysis (new compounds only).
10. 1a: mp  $270^{\circ}$  (dec); IR (KBr)  $2120\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.05 (m, 7H) and 3.55 (m, 6H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 19.7, 25.6, 59.6, 125.5 ppm. Analysis calcd. for  $\text{C}_8\text{H}_{13}\text{N}_3$ : C, 63.5; H, 8.67; N, 27.8. Found: C, 63.3; H, 8.73; N, 28.0.
11. 1b: mp  $71-74^{\circ}$  (dec); IR (KBr),  $2140\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.32 (s) and 3.34 (m, 7 H), 3.80 (d of t) (2 H), 4.14 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 57.1, 61.4, 62.7, 125.2 ppm. Analysis calcd. for  $\text{C}_6\text{H}_{11}\text{N}_3\text{O}$ : C, 51.0; H, 7.85; N, 29.72. Found: C, 50.9; H, 8.00; N, 29.6.
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