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Reaction of Ethyl Chlorosodiocarbamate with Organic Azides

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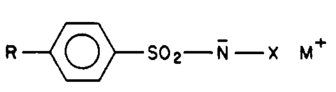
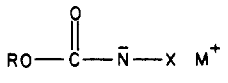
Ethyl chlorosodiocarbamate (**3**) is reactive as a nucleophile toward ethyl azidoformate (**4**) and tosyl azide but not toward alkyl or aryl azides. Diethyl iminodiformate (**5**), nitrogen gas, and sodium chloride are the principal products from the reaction of **3** with **4**. Mechanistic studies support a reaction scheme involving attack of **3** at the carbonyl group of azide **4**, instead of attack at the terminal azido nitrogen. The results of this study are correlated with hard and soft acid and base theory.

The diverse chemistry of *N*-halo-*N*-metallo reagents has been reviewed by Campbell and Johnson,[1] with a major emphasis on the description of *N*-halo-*N*-metallo sulfonamidates (1). Reflecting the lesser amount of work done with the carbamate derivatives, a small portion of the review article described the *N*-halo-*N*-metallocarbamidates (2). As an extension of our previous work with the interaction of organic azides and reactive intermediates,[2] we have examined the nucleophilic reactivity of ethyl chlorosodiocarbamate (**3**) toward organic azides.


1


2

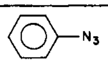
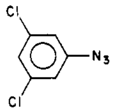
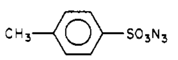
Due to its polar nature[3] ethyl chlorosodiocarbamate (**3**) is soluble in water, methanol, and dimethyl sulfoxide and essentially insoluble in dichloromethane, chloroform, or hexanes. However, salt **3** can be extracted efficiently from water into dichloromethane or from the solid phase into acetonitrile by using a quaternary ammonium phase-transfer catalyst such as tricaprylmethylammonium chloride (Aliquat 336) or cetyltrimethylammonium bromide.[4] The solubility of salt **3** in acetonitrile at room temperature is increased from 3 to 10 mg/mL with the use of 100 mol % of Aliquat 336 (A336). Consequently, we have used A336 as a phase-transfer catalyst in studies designed to explore the nucleophilic reactivity of salt **3** toward organic azides.

As shown in Table I, only ethyl azidoformate and tosyl azide exhibit reactivity toward salt **3** in acetonitrile at room temperature. Methanol dissolves salt **3** but renders it unreactive (expt 5). The presence of A336 is critical for decomposition of tosyl azide in acetonitrile (expts 10 and 11) of ethyl azidoformate in dichloromethane (expts 8 and 9) and enhances decomposition of ethyl azidoformate in acetonitrile (expts 6 and 7).

The reaction of ethyl azidoformate (**4**) and salt **3** produces diethyl iminodiformate (**5**), NaCl, and nitrogen gas as major products (eq 1). The variation of azide decomposition and product distribution with alteration of reaction conditions is displayed in Table II. The efficiency of the reaction of ethyl azidoformate and salt **3** is enhanced by using sufficient A336 to completely dissolve the salt (expts 1 and 4). Apparently, the A336 does not act as a catalyst in the sense of being recycled but instead brings the salt into solution as a quaternary ammonium salt and is not released for further interaction with salt **3**. Makosza has shown that tetraalkylammonium chlorides react with numerous sodium salts to produce the corresponding crystalline tetraalkylammonium salts.[5]

$$\underset{\mathbf{4}}{\mathrm{EtOC(O)N_3}} + \underset{\mathbf{3}}{\mathrm{EtOC(O)\text{-}N^{-}Cl\ Na^{+}}} \rightarrow \underset{\mathbf{5}}{\mathrm{EtOC(O)NHC(O)OEt}} + \mathrm{NaCl} + \mathrm{N_2} \quad (1)$$

Table I. Reactivity of Organic Azides with Ethyl Chlorosodiocarbamate (3)[a]

expt	azide	solvent	catalyst	% azide dec[b]
1		EtOH	none	0
2		CH_3CN	A336	0
3		CH_3CN	A336	0
4	$n\text{-}C_6H_{13}\text{-}N_3$	CH_3CN	A336	0
5	$EtO_2C\text{-}N_3$	MeOH	none	0
6		CH_3CN	none	10
7		CH_3CN	A336	35
8		CH_2Cl_2	none	0
9		CH_2Cl_2	A336	10
10		CH_3CN	none	0
11		CH_3CN	A336	30

[a] Reaction conditions: 2.0 mmol of azide, 2.0 mmol of salt 3, and 0.20 mmol of A336 in 10 mL of solvent; magnetically stirred and protected from light at 25 °C. [b] The percent decomposition was determined by IR analysis after 18-24 h.

More imino compound **5** is produced than azide decomposed when the A336 concentration is limited (expts 1 and 3). These data suggest a source of **5** in addition to the reaction of ethyl azidoformate and salt **3**. In fact, production of **5** is observed when the salt **3** is subjected to the reaction conditions in the absence of azide **4** (expt 2). Although the ethyl chlorosodiocarbamate (**3**) used in this study has a purity greater than 97%, trace amounts of water from the catalyst or solvent could produce equilibrium amounts of ethyl chlorocarbamate (**6**) in a manner similar to that for chloramine T (1; R = CH_3, X = Cl, M = Na).[6] We have found that ethyl chlorocarbamate (**6**) reacts with salt **3** to produce **5** in a manner analogous to

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[1] Campbell, M. M.; Johnson, G. *Chem. Rev.* **1978**, *78*, 65.

[2] (a) Leffler, J. E.; Gibson, H. H., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4117. (b) Gibson, H. H., Jr.; Cast, J. R.; Henderson, J.; Jones, C. W.; Cook, B. F.; Hunt, J. B. *Tetrahdron Lett.* **1971**, 1825. (c) Gibson, H. H., Jr.; Gaddy, H. R., III; Blankenship, C. S. *J. Org. Chem.* **1977**, *42*, 2443.

[3] Saika, D.; Swern, D. *J. Org. Chem.* **1968**, *33*, 4548.

[4] Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977.

[5] Makosza, M.; Bialecka, E. *Synth. Commun.* **1976**, *6*, 313.

[6] Tsujihara, K.; Furukawa, N.; Oae, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2631.

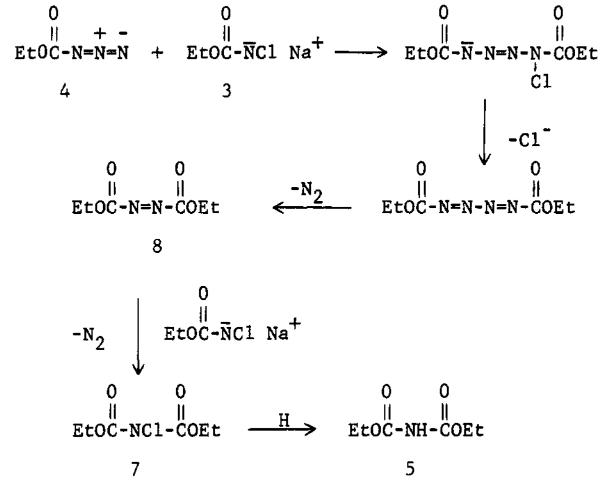
0022-3263/83/1948-2062$01.50/0

Table II. Stoichiometric Data for Reaction of Ethyl Azidoformate (4) and Ethyl Chlorosodiocarbamate (3) in Acetonitrile at 25 °C

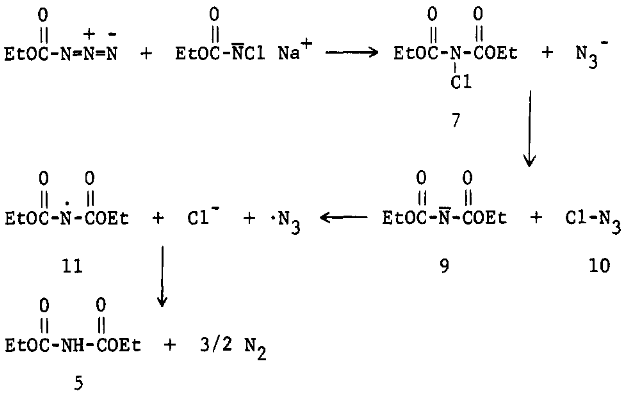
expt	[4], M	[3], M	[A336], M	% azide (4) dec	product yield, % 5[a]	N$_2$[a]	NaCl[b]
1	0.20	0.20	0.04	35[c]	42[c]	60-70[d]	95
2	0.00	0.20	0.04		10[b]		
3	0.20	0.60	0.06	75	113		103
4	0.20	0.20	0.40	90	77		

[a] Based on initial amount of azide 4. [b] Based on initial amount of salt 3. [c] Average value for five experiments. [d] Range of gas production over five experiments.

Scheme I



Scheme II



that reported by Baum for the reaction of ethyl fluorosodiocarbamate with ethyl chlorofluorocarbamate.[7] Thus, eq 2 and 3 suggest a likely source of the excess 5, produced

$$\mathbf{3} + \mathrm{H_2O} \rightleftharpoons \underset{\mathbf{6}}{\mathrm{EtOC(O)NHCl}} + \mathrm{OH^-} \qquad (2)$$

$$\mathbf{6} + \mathbf{3} \rightarrow \underset{\mathbf{7}}{\mathrm{EtOC(O)NClC(O)OEt}} + \mathrm{Na^+NHCl^-} \qquad (3)$$

upon workup from the unstable diethyl *N*-chloroiminodiformate (7).[8]

Although the gas evolution was variable over the range noted (expt 1), the amount of nitrogen produced was consistently greater than the amount of azide decomposed. Consequently, any proposed reaction schemes must include some secondary gas producing reaction subsequent to the decomposition of the azide. The results listed in Tables I and II suggest two possible reaction schemes as shown.

Scheme I depicts attack at the terminal nitrogen of ethyl azidoformate[9] and involves the formation of diethyl azodiformate (8) as an intermediate. When the azo compound 8 is tested as an intermediate by treating it with an equimolar amount of salt 3 under standard reaction conditions, it is partially decomposed (33%) and generates nitrogen gas, the imino compound 5, and sodium chloride (eq 4).

$$\underset{\mathbf{8}\ (2.2\ \mathrm{mmol})}{\mathrm{EtOC(O)N{=}NC(O)OEt}} + \mathbf{3}\ (2.2\ \mathrm{mmol}) \rightarrow \mathbf{5}\ (0.80\ \mathrm{mmol}) + \mathrm{N_2} + \mathrm{NaCl}\ (0.86\ \mathrm{mmol}) \qquad (4)$$

Decomposition of only 33% of the azo compound 8 when treated with an equimolar amount of salt 3 suggests that one should be able to detect or isolate diethyl azodiformate (8) if it were being produced in the reaction between azide 4 and salt 3. However, the use of appropriate GC, TLC, and UV methods failed to detect any diethyl azodiformate (8) from the standard reaction of 4 and 3. In attempts to favor the buildup of the concentration of compound 8 as an intermediate, the standard reaction was run with a tenfold excess of ethyl azidoformate relative to salt 3 and with inverse addition of salt 3. Again, no detectable diethyl azodiformate was produced.

Scheme II, which involves attack on the carbonyl carbon of the azide,[9] proposes the intermediacy of diethyl *N*-chloroiminodiformate (7) and azide ion, which react to produce the imino anion 9 and chlorine azide (10). Neither diethyl *N*-chloroiminodiformate (7) nor azide ion can be detected in product mixtures,[10] but when tested as intermediate, they do react under standard reaction conditions to give diethyl iminodiformate (5), nitrogen gas, and NaCl in the amounts shown (eq 5). The efficiency of this reaction suggests that these intermediates might be formed but not detected within a reaction mixture.

$$\underset{2\ \mathrm{mmol}}{\mathrm{EtOC(O)NClC(O)OEt}} + \underset{2\ \mathrm{mmol}}{\mathrm{Na^+N_3^-}} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{A336}} \underset{1.9\ \mathrm{mmol}}{\mathrm{EtOC(O)NHC(O)OEt}} + \mathrm{N_2} + \mathrm{NaCl}\ (2.8\ \mathrm{mmol}) \qquad (5)$$

Were chlorine azide (10) being produced under the reaction conditions, it would not be stable but would thermally decompose to give gaseous products including nitrogen.[11] Chlorine azide, however, does add to alkenes to give stable addition products such as the products from styrene shown in eq 6,[12] a result which we have confirmed.

$$\underset{\mathbf{9}}{\mathrm{PhCH{=}CH_2}} + \underset{\mathbf{10}}{\mathrm{Cl{-}N_3}} \rightarrow \underset{\mathbf{12}}{\mathrm{PhCH(N_3)CH_2Cl}} + \underset{\mathbf{13}}{\mathrm{PhCHClCH_2{-}N_3}} \qquad (6)$$

Chlorine azide has also been generated from the reaction of *N*-chlorosuccinimide or diethyl *N*-chloroiminodiformate

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[7] Grakaukas, V.; Baum, K. *J. Am. Chem. Soc.* **1969**, *91*, 1679.

[8] Cottrell, S. C.; Abrams, C.; Swern, D. *Org. Prep. Proc.* Int. **1976**, *8*, 25.

[9] Lwowski, W. In "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971; p 529.

[10] Azide ion is detected within product mixtures only when the reaction is run at temperatures above 50 °C.

[11] Cook, R. L.; Gerry, M. C. L. *J. Chem. Phys.* **1970**, *53*, 2525.

[12] Hassner, A.; Boerwinkle, F. *Tetrahedron Lett.* **1969**, 3309.

(7) with sodium azide and again trapped with styrene.[13]

When ethyl azidoformate is treated with ethyl chlorosodiocarbamate in dichloromethane under standard reaction conditions in the presence of equimolar amounts of styrene, a detectable but low yield (less than 5%) of the addition product **12** is produced. Nitrogen gas evolution is slightly decreased by the presence of the styrene, again indicating the trapping of a small amount of chlorine azide.

In the presence of styrene in acetonitrile, chlorine azide (**10**) produces 66% of compound **12**, which arises via free radical intermediates from chlorine azide.[12] As shown in Scheme II, the resulting chlorine free radical oxidizes the imino anion **9** to the corresponding free radical **11** just as the succinimide anion is oxidized to the succinimidyl radical.[14] The azido free radical quantitatively produces nitrogen gas as reported in a study of the electrochemical reduction of azide ion (eq 7).[15] Thus Scheme II is also

$$N_3^- \xrightarrow{-e^-} \cdot N_3 \rightarrow {}^3/_2 N_2 \qquad (7)$$

supported by the amount of nitrogen gas produced in the standard reaction (Table II, expt 1, and eq 5).

As a further test concerning the two possible reaction schemes, we have treated methyl azidoformate (**14**) with salt **3**, isolated the imino products, and determined their composition using quantitative NMR analysis. Scheme I predicts the intermediate formation of ethyl methyl azodicarboxylate (**15**) with subsequent formation of 50% ethyl methyl iminodiformate (**16**) and 50% diethyl iminodiformate (eq 8). Scheme II predicts the formation of only ethyl methyl iminodiformate (eq 9).

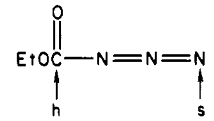
$$\underset{\mathbf{14}}{\mathrm{MeOC(O)N_3}} + \mathrm{EtOC(O)\text{-}N^-ClNa^+} \xrightarrow{\text{Scheme I}} \underset{\mathbf{15}}{\mathrm{MeOC(O)N{=}NC(O)OEt}} \xrightarrow{\mathrm{EtOC(O)\text{-}N^-ClNa^+}} \underset{\mathbf{16}}{\mathrm{MeOC(O)NHC(O)OEt}} + \mathbf{5} \qquad (8)$$

$$\mathbf{14} + \mathrm{EtOC(O)\text{-}N^-ClNa^+} \xrightarrow{\text{Scheme II}} \mathbf{16} \qquad (9)$$

Experimental results reveal the production of 10% diethyl iminodiformate (**5**) and 90% ethyl methyl iminodiformate (**16**). As displayed in Table II, salt **3** undergoes a slow decomposition to produce diethyl iminodiformate (expt 2). These observations from the reaction of methyl azidoformate, then, are consistent with the assumption that the 10% diethyl iminodiformate (**5**) arises from such a decomposition and that the ethyl methyl iminodiformate (**16**) is produced via Scheme II.

In summary, Schemes I and II are compatible with known azide reactivity,[9] suggest viable reaction intermediates, and predict the observed major products. However, the diethyl azodicarboxylate in Scheme I is inefficiently converted into the observed imino compound **5** and is not detectable in the standard reaction mixture. As proposed in Scheme II, diethyl *N*-chloroiminodiformate (**7**) and sodium azide are efficiently converted into **5** and produce nitrogen gas, arising from the thermal decomposition of chlorine azide (**10**), which can be trapped by styrene. Finally, the predominant generation of ethyl methyl iminodiformate (**16**) from methyl azidoformate (**14**) and **3** also lends support to the conclusion that ethyl chlorosodiocarbamate (**3**) reacts with ethyl azidoformate (**4**) via initial attack at the carbonyl group according to the proposed Scheme II.

Ethyl azidoformate and other azidoformates exhibit reactivity toward numerous nucleophiles, including phosphines, carbanions, ylides, amines, and nitrogen-based anions.[9] Attack exclusively at the terminal nitrogen of the azide is observed for phosphines[16] and ylides[17] while carbanion attack has beeen reported for both the terminal nitrogen and the acyl group.[18] For amines[19] and nitrogen-based anions,[9] including the ethyl chlorocarbamate ion of this work, the site of reactivity is the acyl group. Although there is no apparent correlation between site of attack upon the azidoformates and basicity or nucleophilicity of the nucleophiles cited, Pearson's hard and soft acid and base theory does provide a measure of understanding for such observations.[20] Phosphines, ylides, and carbanions are soft bases, while amines and nitrogen-based anions, including ethyl alkylcarbamate anions,[21] are classified as hard bases.[20] Ethyl azidoformate is an ambident electrophile with a hard carbonyl group and a soft terminal nitrogen on the azido group (see below). The mode of reaction of ethyl chlorosodiocarbamate with ethyl azidoformate is in part determined by the hardness of the halocarbamate ion. A systematic study of the effect of solvent, catalyst, and other variables is needed to elucidate other factors controlling such site selection.



$$\underset{\substack{\uparrow \\ h}}{\overset{\substack{O \\ \|}}{\mathrm{EtOC}}} - N = N = \underset{\substack{\uparrow \\ s}}{N}$$

hard and soft acid centers of ethyl azidoformate

This study demonstrates that the ethyl chlorocarbamate anion, under these reaction conditions, is sufficiently nucleophilic to effect displacement upon acyl compounds[22] but not upon alkyl or aryl azides.

Experimental Section

General Methods. Infrared spectrometry was done on a Beckman Acculab 3. GLC analyses were performed on a Varian Aerograph Autoprep 700. ^1H NMR spectra and analyses were obtained from a Varian EM360 with Me_4Si as an internal standard. Melting points were obtained in capillaries on an Electrothermal apparatus and are uncorrected.

Materials. Reagent grade acetonitrile was distilled from either 3-Å molecular sieves or CaH_2.[23] Aliquat 336, tosyl azide, and diethyl azodiformate were purchased from Aldrich. The alkyl[24] and aryl[25] azides, 1-azido-2-chloro-1-phenylethane,[12] azidoformates,[26] ethyl chlorocarbamate,[27] and ethyl chlorosodiocarbamate[28] were prepared by literature methods. Diethyl iminodiformate was purchased (Chemical Procurements Laboratories) and used for the synthesis of diethyl *N*-chloroiminodi-

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[13] The reaction of *N*-chlorosuccinimide with sodium azide has been used as a source of ClN_3: Hassner, A., personal communication. *N*-Bromosuccinimide and sodium azide provide a source of BrN_3: Van Ende, D.; Krief, A. *Angew. Chem.* **1974**, *86*, 311.

[14] Barry, J. E.; Finklestein, M.; Moore, W. M.; Ross, S. D. *J. Org. Chem.* **1982**, *47*, 1292.

[15] Ward, G. A.; Wright, C. M. *J. Electroanal. Chem.* **1964**, *8*, 302.

[16] Leffler, J. E.; Temple, R. D. *J. Am. Chem. Soc.* **1967**, *89*, 5235.

[17] L'abbe, G.; Bestmann, H. *Tetrahedron Lett.* **1969**, 63.

[18] Bertho, A. *J. Prakt. Chem.* **1927**, *116*, 101.

[19] Smith, P. A. S. "Open-Chain Nitrogen Compounds"; W. A. Benjamin: New York, 1966; p 246.

[20] Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3553.

[21] Saville, B. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 936.

[22] Salt **3** also reacts with ethyl chloroformate to produce diethyl *N*-chloroiminodiformate (**7**).

[23] Burfield, D. R.; Lee, K.; Smithers, R. H. *J. Org. Chem.* **1977**, *42*, 3060.

[24] Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2438.

[25] Lieber, E.; Chao, T. S.; Rao, C. N. *J. Org. Chem.* **1957**, *22*, 238.

[26] Lwowski, W.; Mattingly, T. *J. Am. Chem. Soc.* **1965**, *87*, 1947.

[27] Bremner, D. A.; Campbell, M. M.; Johnson, G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1918.

[28] Herranz, E.; Sharpless, K. B. *J. Org. Chem.* **1980**, *45*, 2710.

formate.[8] Ethyl methyl iminodiformate was prepared from methyl chloroformate and salt **3**.[29]

General Method for Reaction of Salt 3 with Azides. To a magnetically stirred suspension of 0.29 g (2.0 mmol) of salt **3** and 0.08 g (0.20 mmol) of A336 in acetonitrile (25 mL) was added 2.0 mmol of the azide. The heterogeneous mixture was stirred at room temperature for 18–24 h and filtered. The residue was washed with acetonitrile, and the organic layers were combined and diluted to the mark in a volumetric flask. For quantitative infrared analysis[30] of azide decomposition, azide stretching frequencies in the range 2090–2190 cm^{-1} were utilized.

Product Study for the Standard Reaction of Salt 3 with Ethyl Azidoformate (4). To a suspension of 0.57 g (4.0 mmol) of salt **3** and 0.326 g (0.8 mmol) of A336 in acetonitrile (10 mL) in a thermostated two-necked flask equipped with a gas buret and a septum was added via a syringe 0.452 g (4.0 mmol) of azide **4** in acetonitrile (10 mL). Gas evolution was essentially complete after 4 h. In experiments designed for qualitative analysis of the evolved gas, the buret was replaced with a collection flask. The gas was analyzed by GLC (6 ft × 0.25 in. column, 5-Å molecular sieves, 55 °C). These conditions provided a separation of N_2, O_2, CO, and CO_2, with only N_2 being detected. The limit for detection of O_2, CO, or CO_2 is 5% yield, based on initial azide **4** concentration. Since the gas was nonoxidizing, Cl_2 was eliminated as a possible constituent.

The heterogeneous reaction mixture was centrifuged and the liquid layer removed. After the pale yellow solid residue was washed twice with acetonitrile, the organic layers were combined, and any residual solvent was removed from the residue. IR analysis of the solid residue via KBr pellet indicated no azide ion or carbonyl-containing compounds. A gravimetric precipitation[31] of chloride ion revealed the production of 0.22 g (3.8 mmol) of NaCl. Removal of solvent from the combined organic layers gave a yellow oil showing one major spot on TLC (Eastman alumina, CH_2Cl_2) due to diethyl iminodiformate (R_f 0.63) and a minor spot due to ethyl carbamate (R_f 0.31). The imino compound **5** was isolated by using flash chromatography[32] on silica gel 60 (400–230 mesh) with ethyl acetate/petroleum ether (2:3) as the eluting solvent. For quantitative analysis, the combined organic layers were diluted to the mark in a volumetric flask for IR analyses at 2125 (ethyl azidoformate) and 1805 cm^{-1} (diethyl iminodiformate).

Reaction of Diethyl Azodiformate (8) with Salt 3. To a suspension of 0.357 g (2.2 mmol) of salt **3** and 0.18 g (0.44 mmol) of A336 in acetonitrile (10 mL) in the apparatus described previously was added 0.415 g (2.3 mmol) of azo compound **8** in acetonitrile (3 mL). The gas and solid analyses were similar to the standard reaction; the IR analysis was done by using a two-component analysis at 1805 and 1240 cm^{-1} for quantitative determination of **5** and **8**.[33]

Reaction of Diethyl *N*-Chloroiminodiformate (7) with NaN_3. To a mixture of 0.131 g (2.0 mmol) of NaN_3, 0.16 g (0.40 mmol) of A336, and acetonitrile (6 mL) in a thermostated, two-necked, round-bottomed flask equipped with a gas buret and an addition funnel was added 0.414 g (2.0 mmol, based on a purity of 94%) of **7** in acetonitrile (13 mL). Gas evolution was complete after 18 h; the gas had no oxidizing power (I_2) and was determined to be nitrogen gas via GLC analysis (5-Å molecular sieve column). The solid and liquid portions were separated as previously described; IR analyses showed no azide ion in the solid but a very small amount dissolved in the organic layer. Quantitative infrared analysis at 1805 cm^{-1} was used for determining the amount of **5** produced.

Reaction of Methyl Azidoformate (14) with Salt 3.[34] In a drybox 0.622 g (4.35 mmol) of salt **3** was added in small portions (0.05 g) at 10-min intervals to a stirred solution of 3.98 g (39.3 mmol) of **14** in acetonitrile (20 mL). Separation of layers and removal of solvent produced a yellow oil, which was taken up in CH_2Cl_2 (20 mL) and washed with 20% $NaHSO_3$ (30 mL). Drying (Na_2SO_4) of the organic layer and removal of solvent and residual azide **14** produced pale yellow crystals having an IR spectrum (CH_2Cl_2; 3420, 1805, 1775, 1735, 1100 cm^{-1}) almost identical with that of ethyl methyl iminodiformate (**16**). Quantitative NMR analysis ($CDCl_3$), which compared the area of the singlet at δ 3.80 (OCH_3 of **16**) with that of the quartet at δ 4.25 (ethoxy CH_2 of **16** and of **5**), indicated 90% of **16** and 10% of **5**.

Studies Designed To Trap ClN_3 (10). (a) From Diethyl *N*-Chloroiminodiformate (7) and NaN_3. To a stirred mixture of 3.03 g (46.0 mmol) of NaN_3, 1.88 g (4.70 mmol) of A336, and 0.36 g (3.5 mmol) of styrene in CH_2Cl_2 (25 mL) at 0 °C was added 1.42 g (7.0 mmol) of **7** in CH_2Cl_2 (5 mL). After 7 h at room temperature, the phases were separated, and the organic layer was concentrated, producing a yellow oil. The presence of 1-azido-2-chloro-1-phenylethane (**12**) was confirmed by IR and TLC (silica gel, 50:50 $CHCl_3/CH_2Cl_2$) analyses, comparing the product mixture with synthesized **12**.[12]

(b) From Salt 3 and Azide 4. To a stirred mixture of 3.02 g (20 mmol) of salt **3**, 1.06 g (10 mmol) of styrene, and 0.81 g (2.0 mmol) of A336 in CH_2Cl_2 at 0 °C was added 2.30 g (20 mmol) of azide **4**. After being stirred for 24 h at room temperature, the reaction mixture was worked up and analyzed by IR and TLC as previously described. Quantitative IR analysis was done at 2100 cm^{-1}.

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Registry No. **3**, 17510-52-0; **4**, 817-87-8; **5**, 19617-44-8; **7**, 29247-18-5; **8**, 1972-28-7; **14**, 1516-56-9; tosyl azide, 941-55-9.

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