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SYNTHESIS OF THIOIMIDATES BY INSERTION OF *TERT*-BUTYLISOCYANIDE INTO THE C-S BOND OF ACTIVATED SULFIDES. REARRANGEMENT OF THIOIMIDATES BY 1,3 C TO N MIGRATION OF AN ALKOXYCARBONYL GROUP.

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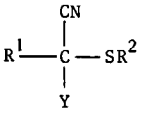
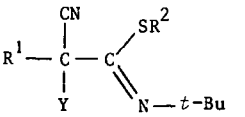
Abstract - *Tert*-butylisocyanide inserts into the carbon-sulfur bond of α-cyano sulfides 2-6 to give thioimidates 10-14. The thioimidates can also be obtained via the chlorine substitution of the *tert*-butylimino chloro sulfides 27-28, which is a more general method. These thioimidates rearrange to E and Z isomers of N-vinylcarbamates 16-20 via a 1,3 C to N migration of the alkoxycarbonyl group.

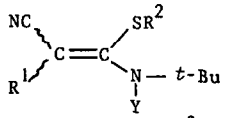
Isocyanides are stable nucleophilic carbenes. They give insertion reactions into carbon-halogen bonds [1,2] or heteroatom-hydrogen bonds [1,3]. These latter reactions can be catalyzed by groups IB and IIB metals and their salts, by acids, or by radical initiators. [1,3] Some uncatalyzed α-addition reactions to N-S bonds,[4] S-H bonds [5] and S-Cl bonds [6,7] are also known. We report here a new uncatalyzed formal insertion of the isocyanide C atom into a carbon-sulfur bond activated by two electronegative groups, one of which is generally a cyano group. [8]



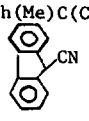
2a-k, Y = CO_2Me R^2 = Me
3a,j, Y = CO_2Me R^2 = Ph
4a,g, Y = CO_2Me R^2 = $PhCH_2$
5a, Y = CO_2Et R^2 = Me
6a, Y = CO_2Et R^2 = $PhCH_2$
7j, Y = COMe R^2 = Me
8l, Y = COPh R^2 = Me
9j, Y = Ph R^2 = Me



10a-e,g, Y = CO_2Me R^2 = Me
11a,e,j, Y = CO_2Me R^2 = Ph
12a, Y = CO_2Me R^2 = $PhCH_2$
13a, Y = CO_2Et R^2 = Me
14a, Y = CO_2Et R^2 = $PhCH_2$
15j, Y = Ph R^2 = Me



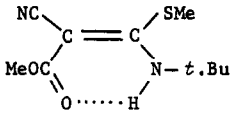
16a-j, Y = CO_2Me R^2 = Me
17j, Y = CO_2Me R^2 = Ph
18a,g, Y = CO_2Me R^2 = $PhCH_2$
19a, Y = CO_2Et R^2 = Me
20a, Y = CO_2Et R^2 = $PhCH_2$
21j, Y = COMe R^2 = Me
22l, Y = COPh R^2 = Me

a, R^1 = $Ph_2C(CN)$
b, R^1 = Ph(Me)C(CN)
c, R^1 = 
d, R^1 = $(PhCH_2)_2C(CN)$
e, R^1 = $PhCH_2$
f, R^1 = p.Cl-C_6H_4
g, R^1 = p.Me-C_6H_4
h, R^1 = p.MeO-C_6H_4
i, R^1 = p.NO_2-C_6H_4
j, R^1 = Ph
k, R^1 = H
l, R^1 = Me

Results and Discussion

The reaction of *tert*-butyl isocyanide 1 with the most reactive sulfides 2-6 was carried out without solvent at room temperature (method A). This method led to a mixture of thioimidates 10-14 and N-vinylcarbamates 16-20 (two isomers Z, E) which were separated by crystallization (Table I). The thioimidates rearranged in solution, at room temperature, to yield the corresponding N-vinylcarbamates, except 11a which is stable under these conditions.

The reaction of *tert*-butyl isocyanide with the less reactive sulfides, slow at room temperature, required heating in acetonitrile (method B) and led to the carbamates 16-18 or amides 21, 22 (Table II). The corresponding thioimidates were not obtained, even by method A, because the rearrangement of these thioimidates is faster than their formation. They were prepared by an alternative procedure (method C). The synthetic precursors, the iminochlorosulfides (27,28), were prepared from the sulfenylchlorides (25, 26) by the insertion reaction of 1 into the S-Cl bond. The iminochlorosulfides 27, 28 were treated *in situ* at room temperature, with the anions derived from 24, to give the thioimidates by a fast reaction (table III). This third method allows isolation of thioimidates or carbamates, which cannot be prepared by methods A and B, as 11e, 15j or 31. Indeed, attempts to insert *t*.BuNC into the carbon-sulfur bond of the sulfides 9j and 30 were unsuccessful.



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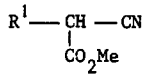

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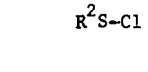
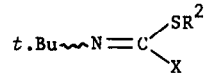
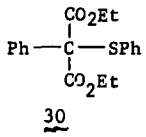


25, R^2 = Me
26, R^2 = Ph



27, X = Cl R^2 = Me
28, X = Cl R^2 = Ph
29, X = Ph(Me)N R^2 = Me



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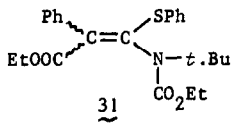

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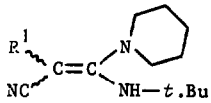

32 d,f,g

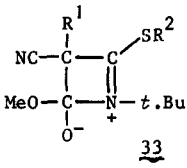

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Table I Insertion of *tert*-butylisocyanide into C-S bond (method A).

Sulfide	Time h [a]	Thioimidate (yield %) [b]	Carbamate (yield %) [b]	Isomer ratio (A/B)
2a	17	10a (40)	16a (40)	72/28
2b	114	10b [c] (45)	16b (10)	67/33
2c	113	10c [c]	16c (82)	55/45
2d	66	10d [c]	16d (60)	64/36
3a	112	11a (84)		
4a	18	12a (75)	18a (6)	70/30
5a	40	13a (34)	19a (37)	70/30
6a	41	14a (43)	20a (29)	95/5

a - Reaction time corresponding to the complete conversion of the starting sulfide in the presence of 3 equiv. of isocyanide. Yield of thioimidate was optimized.
b - Isolated product yield.
c - Observed by NMR. The pure compound was isolated by the method C.

Table II. Insertion of *tert*-butylisocyanide into C-S bond (method B).

Sulfide	Solvent	time h[a]	Product (yield %)[b]	Isomer ratio (E : Z)
2a	CH_2Cl_2	23	16a (88)	69 : 31 [d]
2e	$MeNO_2$	114	16e (20)[c]	
2f	MeCN	7	16f (94)	61 : 39
2g	MeCN	65	16g (89)	62 : 38
2h	MeCN	68	16h (82)	65 : 35
2i	MeCN	87	16i (68)	70 : 30
2j	MeCN	19	16j (85)	60 : 40
3j	MeCN	20	17j (50)	73 : 27
4g	MeCN	22	18g (90)	64 : 36
2k	MeCN	23	23 (45)[c]	
7j	MeCN	16	21j (72)	60 : 40 [d]
8l	MeCN	240	22l (71)	60 : 40 [d]

[a] Reaction time corresponding to the complete conversion of the starting sulfide (except in the case of 2e). [b] Isolated product yield. [c] A single isomer. [d] Isomers A, B.

Table III. Preparation of thioimidate by method C.

Educt	Chloroimine	Product (yield %)
24a	27	10a (68)
24a	28	11a (46)
24c	27	10c (59)
24d	27	10d (42) [a]
24e	27	10e (60) [a]
24e	28	11e (52)
24g	27	10g (39)
24j	28	11j (49)
Ph_2CHCN	27	15j (41)
$PhCH(CO_2Et)_2$	28	31 (32) [b]

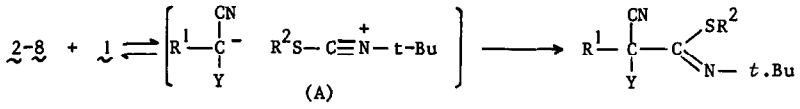
[a] Yield of crude product ; the distillation of 10e gave the carbamate 16e. [b] The carbamate 31 arises from the rearrangement of the corresponding unstable thioimidate.

All isolated thioimidates, amides and carbamates had spectral properties (IR, ^1H NMR) in accord with their assigned structures. A single isomer was isolated for the thioimidates. Two isomers (Z, E) of the N-vinylcarbamates and N-vinyl amides were obtained in most cases.

The structure of the carbamates was confirmed by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of 16g (E and Z) showed a triplet for one olefinic carbon, consistent with a coupling constant $^3J_{C-H}$ with two aromatic protons. More evidence for the structure of the N-vinylcarbamates was obtained from chemical reactivity. The decarbomethoxylation [20] of 16d, 16f and 16g by piperidine in refluxing xylene for 64h gave the corresponding enamines 32, which proves the position of the CO_2Me group in 16. An assignment of structures E, Z is proposed for the N-vinylcarbamates when R^1 is an aryl group. We assum that the *tert*-butyl group, in the prefered conformation of the enamine Z, is shielded by R^1, because the aryl group is not in the plane of the olefinic system for steric reasons.[9] The signal observed in the ^1H NMR spectra for the *tert*-butyl group is shifted to a higher field of $\sim$ 0.6 ppm from E to Z isomer. This assignment was confirmed by the X-ray crystallographic analysis of 16j (Z).[10] When R^1 is not an aryl group, the structures E, Z have not been assigned and the isomers are designated by A and B (Table I). It is interesting to note here that the isomerization E $\rightleftharpoons$ Z of 16-20 is very slow (less than 5 % isomerization after refluxing a pure isomer of carbamate 16g for 64 h in acetonitrile containing 1 % of *tert*-butylisocyanide).

These results show that the conversion of the thioimidates 10-14 is a 1,3-migration of the alkoxycarbonyl group with the formation of the carbamates 16-20. The E isomer is preponderant. The amides 21j and 22l proceed from an 1,3 migration of the acyl group of the corresponding intermediate thioimidates. In the case of 21j, the formation of the Z isomer was preponderant at room temperature. Indeed, when the amides 21j were prepared by the method A, the reaction was slow and the isomer ratio Z/E was 60/40. This reaction was kinetically controlled : a mixture of Z , E isomers of 21j, in the ratio 40 / 60, was obtained by refluxing the pure isomer Z in acetonitrile for 16 h. Under the same conditions, the pure isomer 21j (E) gave a mixture Z , E in the ratio 10 / 90. This isomerisation explains the results given in Table II.

Scheme I



In the case of the sulfide 2k, the reaction with 1 gave the enamine 23E. This isomer is stabilized by an intramolecular hydrogen bond, as detected by infrared spectroscopy.

We propose that first step of the reaction of the sulfides with 1 occurs via the heterolytic and reversible cleavage of the C-S bond of the sulfides, giving an ion pair (A) (Scheme I) according to the following trapping experiment for (A) : treatment of the sulfide 2a with *tert*-butyl isocyanide, at room temperature, in the presence of an excess of N-methylaniline, yielded the cyanoester 24a (70 %) and the isothiourea 29 (one isomer, 83 %).

When the reaction of 1 with a pure diastereoisomer 2b was stopped before the total conversion of the sulfide, the ^{1}H NMR spectrum of the solution showed the formation of one diastereoisomer 10b and a mixture (60:40) of two diastereoisomers 2b. This epimerization of the sulfide 2b is in agreement with the reversible formation of the ion pair (A).

Table IV. ^{1}H NMR estimed first-order rate constants for the rearrangement of thioimidates at 20°C [a].

Thioimidates	Solvent	10^5k, s^{-1}
10a	C_6D_6	0.3
	CD_3CN	1.0
	$CDCl_3$	1.9
10g	C_6D_6	0.5
	CD_3CN	2.4
	$CDCl_3$	3.3
12a	$CDCl_3$	1.1
13a	$CDCl_3$	1.0
14a	$CDCl_3$	0.5

[a] Initial concentration of thioimidate : 0.4M.

The rearrangement of the thioimidates 10-14 is slow in solution at room temperature. Some first-order rate constants are listed in Table IV. This rearrangement is an intramolecular process as demonstrated by the following experiments. A mixture of 12a and 13a, which have rate constants for rearrangement nearly identical, was dissolved in $CDCl_3$ in a 1:1 molar ratio. The products formed were the carbamates 18a and 19a (^{1}H NMR analysis). The cross products 16a and 20a were entirely absent. In the same way, a mixture of 10a and 14a gave the carbamates 16a and 20a ; the carbamates 18a and 19a were not observed.

This thermal rearrangement of the thioimidates to the carbamates or amides is a novel type of rearrangement, formally similar to the known 1,3 O to N acyl shift (Mumm rearrangement of isoimides).[11,12] A rate acceleration is observed when the solvent polarity is increased. These results and the analogy with the known Mumm rearrangement are consistent with the intervention of a four membered dipolar transition state or intermediate as 33.[7,11-14] In $CDCl_3$, 33 is stabilized by solvation (Table IV)

EXPERIMENTAL

Melting points are uncorrected. Mass spectra were obtained on a Varian MAT 311 spectrometer. IR spectra were recorded as suspensions in Nujol, unless otherwise indicated, with a Perkin Elmer 225 spectrometer. NMR spectra (internal standard Me_4Si) were taken in $CDCl_3$ unless stated otherwise, on Bruker WP 80 and FT WP 80 spectrometers. Elemental analyses were performed by the analytical laboratory, Centre National de la Recherche Scientifique.

Materials. *Tert*-Butylisocyanide 1 is a commercial product. Sulfides were obtained from anions of α-cyanoesters, α-cyanoketones or diphenylacetonitrile and N-methylthio, N-benzylthio or N-phenylthiosuccinimide[15,16,21], according to the known procedure.[17]

General Procedure for the Insertion Reactions of Tert-Butyl Isocyanide into C-S Bond of Sulfides. Method A. Isocyanide 1 (15 mmol) was added to the sulfide (2-6) (5 mmol). The mixture was maintained at room temperature for the time indicated in Table I. Then the excess of 1 was evaporated and the residue was analyzed by NMR. Ether was added to this residue to give crystalline thioimidate 10-14. The thioimidate was filtered and the filtrate was concentrated and treated with methanol or ethanol to give crystalline carbamate. *Method B.* To a solution

of 5 mmol of sulfide (2-8) in 15 ml of acetonitrile was added 8 mmol of *tert*-butyl isocyanide. The mixture was refluxed for the time indicated in Table II. Removal of the solvent under reduced pressure gave a mixture of E, Z isomers of carbamates or amides 16-22. These isomers were separated by recrystallization from methanol or ethanol.

Preparation of thioimidates from iminochlorosulfides 27 or 28. Method C. Preparation of a solution of iminochlorosulfides 27 or 28. To a solution of sulfenyl chloride 25 or 26[19] (10 mmol) in tetrahydrofuran (15 ml) was added dropwise, with stirring under N_2, a solution of *tert*-butylisocyanide (0.99 g, 12 mmol) in tetrahydrofuran (15 ml). Immediately the red color of 25 or 26 disappeared. The reaction mixture was stirred for a further 10 min at ambient temperature. *Preparation of thioimidates 10, 11, 15 and carbamate 31.* A solution of triethylammonium salt of 24a, c, d, g, j or of sodium salt of 24e, diphenylacetonitrile and diethylphenylmalonate (10 mmol) in tetrahydrofuran (30 ml) was added to the solution of 27 or 28. The mixture was stirred for 30 min and filtered. Evaporation of the filtrate, extraction of the residue with ether and then crystallization from methanol (or petroleum ether for 10d) give the thioimidate or the carbamate 31.

Methyl 3-tert-Butylimino 2-cyano 2-diphenylcyanomethyl 3-methylthiopropanoate 10a. m.p.147°C IR 1642, 1743, 2236 cm^{-1}. ^1H NMR δ 1.23 (s, 9H), 2.52 (s, 3H), 3.66 (s, 3H), 7.3 (m, 10H). Calcd for $C_{24}H_{25}N_3O_2S$: C, 68.72 ; H, 5.97 ; N, 10.02 ; S, 7.63. Found : C, 68.94 ; H, 6.06 ; N, 10.04 ; S, 7.75.

Methyl 3-tert-Butylimino 2-Cyano 2-(1'-Cyano 1'-phenylethyl) 3-methylthiopropanoate 10b. Only one diastereoisomer was observed. m.p. 93-94°C. IR 1633, 1748, 2223 cm^{-1}. ^1H NMR δ 1.55 (s, 9H), 2.21 (s, 3H), 2.52 (s, 3H), 3.53 (s, 3H), 7.5 (m, 5H). ^{13}C NMR δ 18.3 ($\underline{C}H_3$-S), 24.1 ($\underline{C}H_3$-C-Ph), 28.9 (($\underline{C}H_3)_3C$), 48.0 ($\underline{C}$-CO_2CH_3), 53.8 ($O\underline{C}H_3$), 59.5 (($CH_3)_3\underline{C}$), 67.9 (CH_3-$\underline{C}$-Ph), 115.2, 119.9 ($\underline{C}N$), 144.7 ($\underline{C}$=N), 163.9 (C=O), 127.7 , 128.8 , 129.4 , 135.7 ($\underline{C}_6H_5$). Calcd for $C_{19}H_{23}N_3O_2S$: C, 63.86 ; H, 6.44 ; N, 11.76 ; S, 8.96. Found : C, 63.92 ; H, 6.46 ; N, 11.81 ; S, 8.91.

Methyl 3-Tert-Butylimino 2-cyano 2-(9'-cyanofluorenyl-9') 3-Methylthiopropanoate 10c. m.p. 145°C. IR 1620, 1756, 2230 cm-1. ^1H NMR δ 1.47 (s, 9H), 2.37 (s, 3H), 3.81 (s, 3H), 7.2-8.0 (m, 8H). Calcd for $C_{24}H_{23}N_3O_2S$: C, 69.06 ; H, 5.51 ; N, 10.07 ; S, 7.67. Found : C, 69.00 H, 5.57 ; N, 10.20 ; S, 7.72.

Methyl 3-tert-Butylimino 2-Cyano 2-(dibenzylcyanomethyl) 3-methylthio propanoate 10d. m.p. 110°C. IR 1619, 1734, 2224 cm^{-1}. ^1H NMR δ 1.52 (s, 9H), 2.62 (s, 3H), 3.08, 3.67 (AB, J=14Hz, 1H), 3.18 (s, 2H), 3.30 (s, 3H),7.1-7.5(m,10H).

Methyl 2-benzyl 3-tert-butylimino 2-Cyano 3-methylthiopropanoate 10e. Crude oil ; IR(neat) 1617, 1680, 1745, 2230 cm^{-1}. ^1H NMR δ 1.32 (s, 9H), 2.37 (s, 3H), 3.41 (s, 2H), 3.60 (s, 3H), 7.25 (s, 5H).

Methyl 3-tert-Butylimino 2-Cyano 2-(p.methylphenyl) 3-methylthiopropanoate 10g. m.p. 91°C. IR 1616, 1758, 2231 cm^{-1}. ^1H NMR δ 1.42 (s, 9H), 2.15 (s, 3H), 2.40 (s, 3H), 3.75 (s, 3H), 7.1-7.6 (m, 4H). Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.15 ; H, 6.91 ; N, 8.80 ; S, 10.06. Found : C, 64.18 ; H, 6.89 ; N, 8.77 ; S, 10.20.

Methyl 3-Tert-Butylimino 2-Cyano 2-(Diphenylcyanomethyl) 3-Phenylthiopropanoate 11a. m.p. 130°C. IR 1646, 1750, 2225 cm^{-1}. ^1H NMR δ 1.34 (s, 9H), 3.09 (s, 3H), 7.4 (m, 15H). ^{13}C NMR δ 28.6 (($\underline{C}H_3)_3C$) 53.7 ($O\underline{C}H_3$), 59.0 (($CH_3)_3\underline{C}$), 59.5 (($C_6H_5)_2\underline{C}$), 67.3 ($\underline{C}$-CO_2CH_3), 115.5, 120.5 ($\underline{C}N$), 141.6 ($\underline{C}$=N), 163.2 ($\underline{C}$=O) 127.8 , 128.2 , 129.0 , 129.2 , 129.4 , 129.6, 129.9 , 136.9 , 137.3 , 137.7 ($\underline{C}_6H_5$). Calcd for $C_{29}H_{27}N_3O_2S$: C, 72.34 ; H, 5.61 ; N, 8.73 ; S, 6.65. Found : C, 72.12 ; H, 5.42 ; N, 8.63 ; S, 6.76.

Methyl 2-benzyl-3-tert-butylimino 2-cyano 3-phenylthio propanoate 11e. m.p. 117°C. IR 1624, 1735, 2233 cm^{-1}. ^1H NMR δ 1.50 (s, 9H), 3.15 (s, 3H), 3.40 (m, 2H), 7.2-7.7 (m, 10H). Calcd for $C_{22}H_{24}N_2O_2S$: C, 69.47 ; H, 6.31 ; N, 7.36 ; S, 8.42. Found : C, 69.30 ; H,6.36 ; N, 7.24 ; S, 8.52.

Methyl 3-tert-Butylimino 2-cyano 2-phenyl 3-phenylthiopropanoate 11j. m.p. 94-95°. IR 1614, 1758, 2236 cm^{-1}. ^1H NMR δ 1.48 (s, 9H), 3.69 (s, 3H), 6.8-7.4 (m, 10H). Calcd for $C_{21}H_{22}N_2O_2S$: C, 68.85 ; H, 6.01 ; N, 7.65 ; S, 8.74. Found : C, 68.64 ; H, 6.07 ; N, 7.85; S, 8.79.

Methyl 3-Benzylthio 3-tert-Butylimino 2-Cyano 2-(Diphenylcyanomethyl) propanoate 12a. m.p. 145°C. IR 1640, 1748, 2224 cm^{-1}. ^1H NMR δ 1.27 (s, 9H), 3.69 (s, 3H), 4.24, 4.47 (AB,

J = 12 Hz, 2H), 7.5 (m, 15H). Calcd for $C_{30}H_{29}N_3O_2S$: C, 72.72 ; H, 5.85 ; N, 8.48 ; S, 6.46. Found : C, 72.60 ; H, 5.75 ; N, 8.32; S, 6.25.

Ethyl 3-tert-Butylimino 2-Cyano 2-(Diphenyl-cyanomethyl) 3-Methylthio Propanoate 13a. m.p. 120°C. IR 1639, 1738, 2225 cm^{-1}. ^1H NMR δ 1.17 (t, 3H), 1.26 (s, 9H), 2.53 (s, 3H), 4.17 (m, 2H). Mass spectrum. Exact mass calcd for $C_{25}H_{27}N_3O_2S$ 433.1824, found 433.1837.

Ethyl 3-Benzylthio 3-tert-Butylimino 2-Cyano 2-(Diphenyl cyanomethyl) Propanoate 14a. m.p. 120°C. IR 1635, 1744, 2225 cm^{-1}. ^1H NMR δ 1.16 (t, 3H), 1.28 (s, 9H), 4.17 (m, 2H), 4.19, 4.43 (AB, J = 10 Hz, 2H). Mass spectrum. Exact mass calcd for $C_{31}H_{31}N_3O_2S$ 509.2137, found 509,2114.

3-tert-Butylimino 2,2-Diphenyl 3-Methylthio propionitrile 15j. m.p. 115°C. IR 1608, 1618, 2229 cm^{-1}. ^1H NMR δ 1.27 (s, 9H), 2.17 (s, 3H), 7.30 (s, 10H). Calcd for $C_{20}H_{22}N_2S$ C, 74.53 ; H, 6.83 ; N, 8.69 ; S, 9.93. Found : C, 74.70; H, 6.95 ; N, 8.66 ; S, 10.01.

Methyl N-tert-Butyl N-(2,3-dicyano 3,3-diphenyl 1-methyl thio 1-propenyl) carbamate 16a. *Isomer A*. m.p. 177°C. IR 1548, 1719, 2201, 2229 cm^{-1}. ^1H NMR δ 1.35 (s, 9H), 2.45 (s, 3H), 3.89 (s, 3H), 7.1-7.9 (m, 10H). ^{13}C NMR δ 16.7 ($\underline{C}H_3$-S), 28.2 (($\underline{C}H_3)_3C$), 52.8 ($(CH_3)_3\underline{C}$), 53.0 ($\underline{C}H_3O$), 61.1 (C_3), 116.5, 116.9, 119.7 ($\underline{C}\equiv N$, C_2) 128.3, 129.2, 129.4, 129.5, 135.6, 140.3 ($\underline{C}_6H_5$), 153.4 (C_1), 157.3 (C=O). Anal. calcd for $C_{24}H_{25}N_3O_2S$: C, 68.72 ; H, 5.97 ; N, 10.02 ; S, 7.63. Found : C, 68.80 ; H, 5.94 ; N, 10.01 ; S, 7.72. *Isomer B*. m.p. 148°C. IR 1531, 1715, 2201, 2225 cm^{-1}. ^1H NMR δ 1.62 (s, 9H), 2.17 (s, 9H), 3.79 (s, 3H), 7.4 (br.s, 10H). Calcd for $C_{24}H_{25}N_3O_2S$: C, 68.72 ; H, 5.97 ; N, 10.02 ; S, 7.63. Found : C, 68.86 ; H, 5.76 ; N, 10.18 ; S, 7.76.

Methyl N-tert-Butyl N-(2,3-dicyano 1-methylthio 3-phenyl 1-butenyl) carbamate 16b. *Isomer A*. Observed by NMR in a mixture of isomers A and B. ^1H NMR δ 1.31 (s, 9H), 2.10 (s, 3H), 2.42 (s, 3H), 9.76 (s, 3H). *Isomer B* : m.p. 165°C. IR 1552, 1727, 2207, 2226 cm^{-1}. ^1H NMR δ 1.64 (s, 9H), 2.08 (s, 3H), 2.41 (s, 3H), 3.62 (s, 3H). Calcd for $C_{19}H_{23}N_3O_2S$: C, 63.86 ; H, 6.44 ; N, 11.76 ; S, 8.96. Found : C, 63.88 ; H, 6.50 ; N, 11.98 ; S, 8.84.

Methyl N-tert-Butyl N-(2-cyano 2-(9'-cyanofluorenyl-9') 1-methylthiovinyl) carbamate 16c. *Isomer A*. m.p. 228°C. IR 1554, 1725, 2203, 2228 cm^{-1}. ^1H NMR δ 1.77 (s, 9H), 2.46 (s, 3H), 3.95 (s, 3H), 7.3-7.9 (m, 8H). Calcd for $C_{24}H_{23}N_3O_2S$: C, 69.06 ; H, 5.51 ; N, 10.07 ; S, 7.67. Found : C, 68.92 ; H, 5.49 ; N, 9.85; S, 7.51. *Isomer B*. m.p. 175°C. IR 1531, 1717, 2197 cm^{-1}. ^1H NMR δ 1.55 (s, 9H), 2.04 (s, 3H), 3.67 (s, 3H), 7.3-7.9 (m, 8H). Calcd for $C_{24}H_{23}N_3O_2S$: C, 69.06 ; H, 5.51 ; N, 10.07 ; S, 7.67. Found : C, 68.80 ; H, 5.42 ; N, 10.01 ; S, 7.78.

Methyl N-tert-Butyl N-(3-benzyl 2,3-dicyano 1-methylthio 4-phenyl 1-butenyl) carbamate 16d *Isomer A*. m.p. 156°C. IR 1560, 1729, 2200, 2230 cm^{-1}. ^1H NMR δ 1.16 (s, 9H), 2.34 (s, 3H), 2.95, 3.26 (AB, J = 15 Hz, 2H), 3.16, 3.41 (AB, J = 15 Hz, 2H), 3.57 (s, 3H), 7.4 (m, 10H). ^{13}C NMR δ 17.7 ($\underline{C}H_3$-S), 27.7 (($\underline{C}H_3)_3C$), 43.6, 44.2 (C_6H_5-$\underline{C}H_2$), 47.4 (C_3), 52.8 ($\underline{C}H_3O$), 60.6 (($CH_3)_3\underline{C}$), 116.8 ($\underline{C}N$), 118.7, 118.8 ($\underline{C}N$, C_2), 128.2, 128.3, 128.6, 128.9, 130.8, 131.4, 133.5, 134.0 ($\underline{C}_6H_5$), 153.5 (C_1), 155.8 ($\underline{C}$=O). Calcd for $C_{26}H_{29}N_3O_2S$: C, 69.79 ; H, 6.51 ; N, 9.39 ; S, 7.15. Found : C, 70.09 ; H, 6.30; N, 9.24 ; S, 7.29. *Isomer B*. m.p. 125°C. IR 1532, 1715, 2197, 2228 cm^{-1}. ^1H NMR δ 1.40 (s, 9H), 2.15 (s, 3H), 3.25, 3.41 (AB, J = 17 Hz, 2H), 3.27 (s, 2H), 3.60 (s, 3H), 7.4 (m, 10H). Calcd for $C_{26}H_{29}N_3O_2S$: C, 69.79 ; H, 6.51 ; N, 9.39 ; S, 7.15. Found : C, 69.80; H, 6.48 ; N, 9.57 ; S, 7.13.

Methyl N-tert-Butyl N-(2-cyano 1-methylthio 3-phenyl 1-propenyl) carbamate 16e. One isomer, m.p. 73-74°C (hexane). IR 1567, 1704, 2204 cm^{-1}. ^1H NMR δ 1.53 (s, 9H), 2.32 (s, 3H), 3.36, 3.67 (AB, J = 15 Hz, 2H), 3.59 (s, 3H), 7.2 (br.s, 5H). Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.15 ; H, 6.91 ; N, 8.80 ; S, 10.06. Found : C, 63.41 ; H, 6.97 ; N, 8.68 ; S, 10.19.

Methyl N-tert-Butyl N-((2-p.chlorophenyl 2-cyano 1-methylthio) vinyl) carbamate 16f. *Isomer E* observed by NMR in a mixture of isomers E and Z. ^1H NMR δ 1.66 (s, 9H), 2.18 (s, 3H), 3.76 (s, 3H). *Isomer Z* : m.p. 114°C. IR 1570, 1716, 2200 cm^{-1}. ^1H NMR δ 1.20 (s, 9H), 2.46 (s, 3H), 3.83 (s, 3H), 7.3 (m, 4H). Calcd for $C_{16}H_{19}ClN_2O_2S$: C, 56.72 ; H, 5.61; Cl, 10.48 ; N, 8.27 ; S, 9.45. Found : C, 56.76 ; H, 5.85 ; Cl, 10.72 ; N, 8.11 ; S, 9.30.

Methyl N-tert-Butyl N-(2-cyano 2-p.methylphenyl 1-methylthio) vinyl) carbamate 16g. Isomer E. m.p. 81°C. IR 1552, 1717, 2195 cm^{-1}. ^1H NMR δ 1.65 (s, 9H), 2.14 (s, 3H), 2.38 (s, 3H), 3.75 (s, 3H), 7.3 (m, 4H). ^{13}C NMR δ 15.5 ($\underline{C}H_3$-S), 21.4 ($\underline{C}H_3$-C_6H_4), 28.7 (($\underline{C}H_3)_3C$), 52.9 ($\underline{C}H_3O$), 60.8 ($(CH_3)_3\underline{C}$), 114.8 (C_2), 118.1 ($\underline{C}\equiv N$), 129.0, 129.4, 129.5, 139.7 ($\underline{C}_6H_4$), 153.9 (C_1), 154.0 ($\underline{C}$=O). Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.15; H, 6.92 ; N, 8.80 ; S, 10.06. Found : C,64.30; H, 6.99 ; N, 8.88 ; S, 9.90. *Isomer Z.* m.p. 154-155°C. IR 1557, 1710, 2196 cm^{-1}. ^1H NMR δ 1.18 (s, 9H), 2.34 (s, 3H), 2.44 (s, 3H), 3.81 (s, 3H), 7.14 (s, 4H). ^{13}C NMR δ 16.2 ($\underline{C}H_3$-S), 21.4 ($\underline{C}H_3$-C_6H_4), 28.1 (($\underline{C}H_3)_3C$), 52.7 ($\underline{C}H_3O$), 60.2 ($(CH_3)_3\underline{C}$), 113.8 (C_2), 117.9 ($\underline{C}\equiv N$), 128.3, 129.7, 130.6, 139.4 (C_6H_4), 153.7 (C_1), 154.2 ($\underline{C}$=O). Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.15 ; H, 6.92 ; N, 8.80 ; S, 10.06. Found : C, 63.88 ; H, 6.94 ; N, 9.02 ; S, 10.16.

Methyl N-tert-Butyl N-((2-cyano 2-p-methoxyphenyl 1-methylthio) vinyl) carbamate 16h. Mixture of isomers E and Z. m.p. 99-101°C, IR 1550, 1602, 1716, 2202 cm^{-1}. *Isomer E* ^1H NMR δ 1.64 (s, 9H), 2.14 (s, 3H), 3.72 (s, 3H), 3.78 (s, 3H), 6.7-7.5 (m, 4H). *Isomer Z* ^1H NMR δ 1.18 (s, 9H), 2.42 (s, 3H), 3.80 (s, 6H), 6.7-7.5 (m, 4H). Calcd for $C_{17}H_{22}N_2O_3S$: C, 61.07 ; H, 6.58 ; N, 8.38 ; S, 9.58. Found : C, 61.70 ; H, 6.48 ; N, 8.05 ; S, 8.54.

Methyl N-tert-Butyl N-((2-cyano 1-methylthio 2-p.nitrophenyl)vinyl) carbamate 16i. Mixture of isomers E and Z. m.p. 109-111°C. IR 1589, 1596, 1718, 1727, 2195, 2207 cm^{-1}. *Isomer E,* ^1H NMR δ 1.68 (s, 9H), 2.26 (s, 3H), 3.80 (s, 3H), 7.5-8.6 (m, 4H). *Isomer Z* ^1H NMR δ 1.20 (s, 9H), 2.53 (s, 3H), 3.88 (s, 3H), 7.5-8.6 (m, 4H). Calcd for $C_{16}H_{19}N_3O_4S$: C, 55.01 ; H, 5.44 ; N, 12.03. Found : C, 55.11 ; H, 5.39; N, 12.03.

*Methyl N-tert-Butyl N-((2-cyano 1-methylthio 2-phenyl)vinyl) carbamate 16j. Isomer E.*m.p. 99-100°C. IR 1552, 1575, 1715, 2203 cm^{-1}. ^1H NMR δ 1.67 (s, 9H), 2.15 (s, 3H), 3.76 (s, 3H), 7.4 (m, 5H). Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.15; H, 6.57 ; N, 9.21 ; S, 10.52. Found : C, 62.91; H, 6.53 ; N, 9.10 ; S, 10.41. *Isomer Z.* m.p. 106°C. IR 1550, 1570, 1702, 2202 cm^{-1}. ^1H NMRδ 1.17 (s,9H), 2.45 (s, 3H), 3.83 (s, 3H), 7.35 (s, 5H). Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.15 ; H, 6.57 ; N, 9.21 ; S, 10.52. Found : C,62.92; H, 6.68 ; N, 9.22 ; S, 10.44.

Methyl N-tert-Butyl N((2-cyano 2-phenyl 1-phenylthio) vinyl) carbamate 17j. Isomer E. m.p. 67-68°C. IR 1555, 1720, 2199 cm^{-1}. ^1H NMR δ 1.47 (s, 9H), 3.76 (s, 3H), 7.3 (m, 10H). Calcd for $C_{21}H_{22}N_2O_2S$: C, 68.85 ; H, 6.01 ; N, 7.65 ; S, 8.74. Found : C, 68.92 ; H,6.13; N, 7.89 ; S, 8.68. *Isomer Z* (this compound was not purified). ^1H NMR δ 0.95 (s, 9H), 3.66 (s, 3H), 7.0-7.5 (m, 10H).

Methyl N-tert-Butyl N-(1-benzylthio 2,3-dicyano 3,3-diphenyl 1-propenyl) carbamate 18a. Isomer A. m.p. 192°C. IR 1540, 1722, 2202, 2234 cm^{-1}. ^1H NMR δ 1.37 (s, 9H), 3.70 (s, 3H), 4.14, 4.27 (AB, J = 12 Hz, 2H), 7.4 (m, 15H). Calcd for $C_{30}H_{29}N_3O_2S$: C, 72.72 ; H, 5.85 ; N, 8.48 ; S, 6.46. Found : C, 72.95 ; H, 5.90; N, 8.43 ; S, 6.48. *Isomer B* (in a mixture of A and B). ^1H NMR δ 1.68 (s, 9H), 3.71 (s, 3H), 3.91 (s, 2H).

Methyl N-tert-Butyl N-((1-benzylthio 2-cyano 2-p.methylphenyl) vinyl) carbamate 18g. Isomer E. m.p. 100°C. IR 1571, 1710, 2203 cm^{-1}. ^1H NMR δ 1.70 (s, 9H), 2.34 (s, 3H), 3.69 (s, 3H), 3.84 (s, 2H), 7.0-7.5 (m, 9H). Calcd for $C_{23}H_{26}N_2O_2S$: C, 70.05 ; H, 6.59 ; N, 7.10 ; S, 8.12. Found : C, 69.75 ; H, 6.53 ; N, 7.26; S, 8.28. *Isomer Z.* m.p. 130°C. IR 1552, 1710, 2198 cm^{-1}. ^1H NMR δ 1.21 (s, 9H), 2.34 (s, 3H), 3.73 (s, 3H), 4.16, 4.33 (AB, J = 12 Hz, 2H), 7.3 (m, 9H). Calcd for $C_{23}H_{26}N_2O_2S$: C, 70.05; H, 6.59 ; N, 7.10 ; S, 8.12. Found : C, 70.08; H, 6.56 ; N, 7.21 ; S, 8.20.

Ethyl N-tert-Butyl N-(2,3-dicyano 3,3-diphenyl 1-methylthio 1-propenyl) carbamate 19a. Isomer A. m.p. 179°C. IR 1551, 1712, 2206, 2231 cm^{-1}. ^1H NMR δ 1.35 (s, 9H), 1.41 (t, J = 7 Hz, 3H), 2.48 (s, 3H), 4.35 (q, J = 7Hz, 2H), 7.1-7.8 (m, 10H). Calcd for $C_{25}H_{27}N_3O_2S$: C, 69.28 ; H, 6.23 ; N, 9.69 ; S, 7.39. Found: C, 69.33 ; H, 6.29 ; N, 9.66 ; S, 7.16. *Isomer B.* m.p. 145°C. IR 1514, 1712, 2201, 2230 cm^{-1}. ^1H NMR δ 1.38 (t, J = 7 Hz, 3H), 1.62 (s, 9H), 2.22 (s, 3H), 4.26 (m, 2H), 7.4 (m, 10H). Calcd for $C_{25}H_{27}N_3O_2S$: C, 69.28 ; H, 6.23 ; N, 9.69 ; S, 7.39. Found : C, 69.05 ; H, 6.25 ; N, 9.70 ; S, 7.20.

Ethyl N-tert-Butyl N-(1-benzylthio 2,3-dicyano 3,3-diphenyl 1-propenyl) carbamate 20a. Isomer A. m.p. 139-140°C. IR 1551, 1713, 2205, 2227 cm^{-1}. ^1H NMR δ 1.37 (t, J = 7 Hz, 3H), 1.39 (s, 9H), 4.32 (m, 2H), 4.19, 4.41 (AB, J = 12 Hz, 2H), 7.2-7.9 (m, 15H). Calcd for

$C_{31}H_{31}N_3O_3S$: C, 73.08 ; H, 6.09 ; N, 8.25 ; S, 6.28. Found : C, 73.33 ; H, 6.08 ; N, 8.02; S, 5.99. *Isomer B* (in a mixture of A and B) ^1H NMR δ 1.69 (s, 9H), 3.96 (s, 2H).

N-tert-Butyl N-(2-cyano 1-methylthio 2-phenyl) vinyl acetamide 21j. Isomer Z. m.p. 127°C. IR 1537, 1662, 2202 cm^{-1}. ^1H NMR δ 1.23 (s, 9H), 2.35 (s, 3H), 2.55 (s, 3H), 7.37 (s, 5H). Calcd for $C_{16}H_{20}N_2OS$: C, 66.66 ; H, 6.94 ; N, 9.72 ; S, 11.11. Found : C, 66.40 ; H, 7.01 N, 9.86 ; S, 11.22. *Isomer E.* m.p. 123-124°C. IR 1546, 1661, 2197 cm^{-1}. ^1H NMR δ 1.68 (s, 9H), 2.18 (s, 3H), 2.22 (s, 3H); 7.47 (s, 5H). Calcd for $C_{16}H_{20}N_2OS$: C, 66.66 ; H, 6.94 ; N, 9.72 ; S, 11.11. Found : C, 66.39 ; H, 6.89 ; N, 9.93 ; S, 11.16.

N-tert-Butyl N-(2-cyano 1-methylthio 1-propenyl)benzamide 22l. Oil, mixture of isomers A and B. IR (neat) 1572, 1656, 2200 cm^{-1}. *Isomer A.* ^1H NMR δ 1.68 (s, 9H), 1.76 (s, 3H), 2.26 (s, 3H), 7.3 (m, 5H). *Isomer B.* ^1H NMR δ 1.60 (s, 9H), 1.98 (s, 3H), 2.26 (s, 3H), 7.3 (m, 5H). Calcd for $C_{16}H_{20}N_2OS$: C, 66.66 ; H, 6.94 ; N, 9.72 ; S, 11.11. Found : C,66,85; H, 7.14 ; N, 9.86 ; S, 10.86.

Methyl 3-tert-Butylamino 2-cyano 3-methylthio acrylate 23E. m.p. 92°C. IR (CCl_4) 1656, 2202, 3180 cm^{-1}. ^1H NMR δ 1.54 (s, 9H), 2.70 (s,3H), 3.75 (s, 3H), 10.35 (br.s, 1H). Calcd for $C_{10}H_{16}N_2O_2S$: C, 52.63 ; H, 7.01 ; N, 12.28 ; S, 14.03. Found : C, 52.62 ; H, 7.09 ; N, 12.30 ; S, 14.06.

Ethyl N-tert-Butyl N-((2-Ethoxycarbonyl 2-phenyl 1-phenylthio) vinyl) carbamate 31. One purified isomer (E or Z). m.p. 60-62°C (cyclohexane) IR 1566, 1573, 1715 cm^{-1}. ^1H NMR δ 1.16 (t, J = 7 Hz, 3H), 1.29 (t, J = 7 Hz,3H), 1.35 (s, 9H), 4.09 (m, 4H), 7.0-7.5 (m, 10H). Calcd for $C_{24}H_{29}NO_4S$: C, 67.44 ; H, 6.79 ; N, 3.27 ; S, 7.49. Found : C, 67.33 ; H,6.81; N, 3.27 ; S, 7.75.

Reaction of carbamates with piperidine. To a solution of carbamate 16 (mixture of E, Z isomers) (3 mmol) in 30 ml of xylene, was added 2 ml of piperidine. After being refluxed for 64 h, the solution was evaporated and the residue was treated with ether (10 ml). The enamine 32 was filtered and purified by crystallization from ethanol.

3-Benzyl 1-tert-Butylamino 2,3-dicyano 4-phenyl 1-(N-piperidinyl) 1-butene 32d. 0,46 g (36 %) m.p. 164°C (EtOH). IR 1555, 2171, 2223, 3387 cm^{-1}. ^1H NMR δ 0.89 (s, 9H), 1.50 (br.s, 6H), 2.73 (br.s, 1H), 2.89 (br.s, 4H), 3.19 (s, 4H), 7.2-7.6 (m, 10H). Calcd for $C_{28}H_{34}N_4$: C, 78.87 ; H, 7.98 ; N, 13.14. Found : C, 78.66 ; H, 8.08 ; N, 12.90.

1-tert-Butylamino 2-p.chlorophenyl 2-cyano 1-(N-piperidinyl)ethene 32f. 0.85 g (87 %) m.p. 161°C (EtOH). IR 1534, 2146, 3325 cm^{-1}. ^1H NMR δ 1.36 (s, 9H), 1.55 (br.s, 6H), 3.00 (br. s, 4H), 3.97 (br.s, 1H). Calcd for $C_{18}H_{24}ClN_3$: C, 68.03 ; H, 7.55 ; N, 13.22 ; Cl, 11.18. Found : C, 68.00 ; H, 7.60 ; N, 13.51 ; Cl, 11.41.

1-tert-Butylamino 2-cyano 2-p.methylphenyl 1-(N-piperidinyl)ethene 32g. 0.60 g (67 %) m.p. 121°C (EtOH). IR 1532, 2154, 3331 cm^{-1}. ^1H NMR δ 1.37 (s, 9H), 1.55 (br.s, 6H), 2.32 (s, 3H), 3.02 (br.s, 4H), 3.95 (br.s, 1H), 7.02 (s, 4H). Calcd for $C_{19}H_{27}N_3$: C, 76.76 ; H, 9.09 ; N, 14.14. Found C, 76.60 ; H, 9.20; N, 14.21.

Trapping of the ion pair (A) with N-methylaniline. A mixture of sulfide 2a (1.68 g, 5 mmol), isocyanide 1 (1.24 g, 15 mmol) and N-methylaniline (3.21 g, 30 mmol) was stirred at ambient temperature for 18 h. The excess of N-methylaniline and isocyanide was evaporated. The residue, treated with a mixture of ether-petroleum ether, gave the ester 24a which was filtered. The filtrate was evaporated to give the isothiourea 29 (0.98 g, 83 %). bp 80° (0.02 mm). ^1H NMR δ 1.37 (s, 9H), 2.03 (s, 3H), 3.12 (s, 3H), 6.9-7.6 (m, 5H). Calcd for $C_{13}H_{20}N_2S$: C, 66.10 ; H, 8.47 ; N, 11.86; S, 13.55. Found, C, 66.30 ; H, 8.33 ; N,11.17; S, 13.35.

Rearrangement of a mixture of thioimidates. Thioimidates 12a (49 mg, 0.1 mmol) and 13a (43 mg, 0,1 mmol) were dissolved in $CDCl_3$ (0.5 ml) and the solution was analyzed by ^1H NMR. A mixture of 10a (42 mg, 0.1 mmol) and 14a (51 mg, 0.1 mmol) in $CDCl_3$ (0.5 ml) was analyzed in the same manner. The normal rearranged products were observed, without cross products.

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