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STUDIES ON VINYL ISOCYANIDES

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Abstract - The vinyl isocyanides 2,4,6-$(CH_3)_3C_6H_2CH$=CHNC and $(CH_3)_3CCH$=CHNC and the new 1,3-dienyl isocyanide CH_3CH=$CH(CH_3)$-CH=CHNC have been prepared from the corresponding aldehydes and methyl isocyanide using a method first developed by Schöllkopf, Stafforst, and Jentsch [5] The new vinyl isocyanides $(CH_3)_2C$=CHNC and CH_3CH=$C(CH_3)NC$ have been prepared by the Cu_2O-catalyzed isomerization of the corresponding allyl isocyanides The liquid vinyl isocyanides may be characterized by the formation of solid cis-$(RNC)_2Mo(CO)_4$ derivatives through reaction with norbornadienetetracarbonylmolybdenum in hexane solution at ambient temperature Examination of these molybdenum carbonyl complexes by proton and carbon-13 NMR spectroscopy indicates that the isocyanide carbon atom but not the carbon-carbon double bond of the vinyl isocyanide ligands is bonded to the molybdenum atom The proton-decoupled carbon-13 NMR spectra of the vinyl isocyanides, but not their molybdenum carbonyl complexes, indicate coupling of the isocyanide nitrogen to both the isocyanide carbon (^1J(C-N)=6 Hz) and the vinyl carbon bearing the isocyanide group (^1J(C-N)=11-13 Hz) leading to 1 1 1 triplets for these resonances These vinyl carbonyl resonances are used to estimate the cis-trans isomer ratios in vinyl isocyanides of the type RCH=CHNC Such studies suggest that the formation of vinyl isocyanides by the copper(I) catalyzed isomerization of the corresponding allylic isocyanides is more nearly stereospecific than the formation of vinyl isocyanides by the elimination reaction of the Schollkopf/Stafforst/Jentsch synthetic method

INTRODUCTION

Recent research from this laboratory has extended the preparation of poly(iminomethylenes)[1,2,3] to systems having pendant carbon-carbon double bonds For this research we needed a variety of vinyl isocyanides containing alkyl and aryl substituents in various positions However, at the start of this project known information on the synthesis of vinyl isocyanides was rather limited Unsubstituted vinyl isocyanide was first reported by Matteson and Bailey in 1968 [4] The most generally applicable methods for the synthesis of substituted vinyl isocyanides appear to be that of Schöllkopf, Stafforst, and Jentsch[5] involving the reaction of lithiated methyl isocyanide with carbonyl compounds followed by dehydration and that of Saegusa, Murase, and Ito[6] involving the copper(I) catalyzed isomerization of the corresponding allyl isocyanides Vinyl isocyanides have also been obtained by reactions of aldehydes or ketones with metallated isocyanides containing dialkoxyphosphoryl[7,8] or arylsulfonyl[9] groups The synthesis of vinyl isocyanides is of importance not only because of their polymerization to give poly(iminomethylenes) with potentially interesting properties but also because of their relationship to the antibiotic xanthocillin [10,11]

This paper describes applications of both the Schöllkopf/Stafforst/Jentsch and the Saegusa/Murase/Ito vinyl isocyanide syntheses to the preparation of new vinyl isocyanides having interesting structures and properties New vinyl isocyanides described in this paper include 2,4,6-$(CH_3)_3C_6H_2CH$=CHNC, the first crystalline vinyl isocyanide containing only hydrocarbon substituents, CH_3CH=$C(CH_3)$-CH=CHNC, the first example of a 1,3-dienyl monoisocyanide, and the direct synthesis of CH_3CH=$C(CH_3)NC$, a vinyl isocyanide bearing an alkyl group on the same carbon bearing the isocyanide group In addition this paper describes a new method for characterizing relatively sensitive liquid vinyl isocyanides as their crystalline molybdenum carbonyl derivatives of the type cis-$(RNC)_2Mo(CO)_4$ by reaction with norbornadienetetracarbonylmolybdenum

EXPERIMENTAL SECTION

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Georgia Melting and decomposition points were determined in capillaries and are uncorrected Infrared spectra were recorded on a Perkin-Elmer Model 599B spectrometer Proton NMR spectra were recorded on a Varian T-60 spectrometer operating at a nominal frequency of 60 MHz or a Varian EM-390 spectrometer operating at a nominal frequency of 90 MHz Carbon-13 NMR spectra were recorded on a JEOL FX-90Q spectrometer operating in the pulsed Fourier transform mode at a nominal frequency of 22 5 MHz with proton noise decoupling Proton and carbon-13 NMR chemical shifts are reported in p p m downfield from internal tetramethylsilane

The isocyanides CH_3NC (ref 12), $CH_3CH{=}CHNC$ (ref 6), and $C_6H_5CH{=}CHNC$ (ref 5), the amines $CH_2{=}C(CH_3)CH_2NH_2$ and $CH_2{=}CHCH(CH_3)NH_2$ (ref 13), and the norbornadiene complex (nor-C_7H_8)$Mo(CO)_4$ (ref 14) were prepared by the cited published procedures Other reagents were standard commercial products, purchased mainly from Aldrich Chemical Company, Milwaukee, Wisconsin Solvents were redistilled under nitrogen before use, sodium benzophenone ketyl was used as the drying agent for ethers All experiments were done in a well-ventilated hood using methanolic hydrochloric acid to trap noxious isocyanide vapors

Preparation of $(CH_3)_3CCH{=}CHNC$

A solution of 12 9 g (290 mmoles) of methyl isocyanide in 300 ml of tetrahydrofuran was placed in a 2-liter 3-neck flask fitted with a low temperature thermometer, motor stirrer, dropping funnel, and nitrogen inlet After cooling in a dry ice-acetone bath, the methyl isocyanide solution was treated with 182 ml (291 mmoles) of 1 6 N n-butyllithium in hexane at such a rate that the temperature of the reaction mixture did not exceed -65°C After stirring for an additional 5 minutes, the resulting cold solution of isocyanomethyllithium was treated with a solution of 24 5 g (285 mmoles) of pivalaldehyde (trimethylacetaldehyde) in 110 ml of tetrahydrofuran at such a rate that the temperature continued to stay below -65°C After stirring for an additional 10 minutes, the reaction mixture was next treated with a solution of 55 0 g (288 mmoles) of p-toluenesulfonyl chloride in 140 ml of tetrahydrofuran The reaction mixture was kept below -65°C for an additional 15 minutes after the addition of the p-toluenesulfonyl chloride was complete The dry ice bath was then removed and the reaction mixture was allowed to warm to +30-35°C At this temperature a solution of 25 0 g (390 mmoles) of 87 5% potassium hydroxide in 110 ml of methanol was added over a period of 45 minutes After stirring for an additional 45 minutes, the solvents (tetrahydrofuran, hexane, and methanol) were removed in a water aspirator vacuum and trapped at -78°C The residue was treated with 400 ml of water and the resulting mixture was extracted with four 150 ml portions of diethyl ether The diethyl ether extracts were dried over anhydrous magnesium sulfate at -20°C Diethyl ether was removed from the filtered extracts by distillation at atmospheric pressure leaving some of the crude $(CH_3)_3CCH{=}CHNC$ as a less volatile residue Similarly, the trapped reaction solvents were also distilled at atmospheric pressure leaving more of the $(CH_3)_3CCH{=}CHNC$ as a less volatile residue Vacuum distillation of the combined $(CH_3)_3CCH{=}CHNC$ gave 21 2 g (86% yield) of the pure product, b p 41°C/10 mm , proton NMR in $CDCl_3$ δ6 16 (1H, doublet of triplets, J(H-H)=14 Hz , J(N-H)=4 Hz), δ 5 59 (1H, doublet of triplets, J(H-H)=14 Hz , J(N-H)=2 Hz), and δ1 05 (9H, singlet), proton-decoupled carbon-13 NMR in $CDCl_3$ δ162 4 (NC triplet, J(N-C)=6 Hz) , δ149 2(=CH singlet), δ109 5 (=CH triplet, J(N-C)=13 Hz), δ 29 2 (C singlet) and δ 28 7 (CH_3 singlet), infrared spectrum in $CHCl_3$ ν (CH) at 3000 (m), 2950 (vs), 2907 (m), and 2807 (s) cm $^{-1}$, ν(CN) at 2125 (vs) cm $^{-1}$, ν(C=C) at 1630 (m) cm $^{-1}$, other bands at 1475 (s), 1462 (s), 1390 (m), 1363 (s), 1267 (m), 1222 (m), 1204 (s), 1105 (s), 1070 (m), 1043 (s), 997 (s), 950 (s), 943 (s), and 920 (m) cm $^{-1}$

Preparation of cis-$[(CH_3)_3CCH{=}CHNC]_2Mo(CO)_4$

A solution of 0 605 g (2 0 mmoles) of (nor-C_7H_8)$Mo(CO)_4$ in 50 ml of hexane was treated with 2 0 g (18 4 mmoles) of $(CH_3)_3CCH{=}CHNC$ The reaction mixture became turbid after stirring for 15 minutes at room temperature Some product precipitated after standing overnight, additional product precipitated upon concentration and cooling to -10°C to give a total of 0 210 g (24% yield) of crude cis-$[(CH_3)_3CCH{=}CHNC]_2Mo(CO)_4$ The analytical sample, dec 192°C, was purified by crystallization from a mixture of dichloromethane and hexane, proton NMR in $CDCl_3$ δ6 15 (1H, doublet, J=14 Hz), δ5 77 (1H, doublet, J=14 Hz), and δ 1 07 (9H, singlet), proton-decoupled carbon-13 NMR in $CDCl_3$ δ209 5 (CO), δ 206 0 (CO), NC not observed, δ147 9 (=CH), δ110 8 (=CH), δ32 8 (C), and δ28 8 (CH_3), infrared spectrum in CH_2Cl_2 ν (CH) bands at 2960 (s), 2905 (w), and 2867 (w) cm $^{-1}$, ν(CN) bands at 2150 (m), 2125 (w), and 2100 (m) cm $^{-1}$, ν (CO) bands in hexane at 2008 (s), 1966 (s), 1953 (vs), and 1943 (vs) cm $^{-1}$, other bands at 1680 (w), 1630 (w), 1473 (m), 1460 (m), 1364 (m), 1360 (m), 1303 (w), 1251 (w), 941 (s), 690 (s), and 591 (s) cm $^{-1}$, anal calcd for $C_{18}H_{22}MoN_2O_4$ C, 50 7, H, 5 2, N, 6 6 Found C, 50 4, H, 5 3, N, 6 5

Preparation of 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$

A procedure analogous to the preparation of $(CH_3)_3CCH{=}CHNC$ above was followed using in sequence a solution of 7 547 g (183 mmoles) of methyl isocyanide in 300 ml of tetrahydrofuran, 68 ml (184 mmoles) of 2 7 M n-butyllithium in hexane plus an additional 40 ml of hexane, 25 0 g (169 mmoles) of mesitaldehyde, 2,4,6-$(CH_3)_3C_6H_2CHO$, in 75 ml of tetrahydrofuran, 33 0 g (173 mmoles) of p-toluenesulfonyl chloride in 110 ml of tetrahydrofuran, and 17 1 g (265 mmoles) of 87% potassium hydroxide in 75 ml of methanol In this case removal of diethyl ether from the extracts gave a solid which could be crystallized from a mixture of diethyl ether and hexane to give a total of 11 9 g (41% yield) of 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$, m p 92-94°C, proton NMR in $CDCl_3$ δ7 00 (1H, doublet, J=15 Hz), δ6 86 (2H, singlet), δ5 82 (1H, doublet, J=15 Hz), and δ 2 25 (9H, singlet), proton-decoupled carbon-13 NMR in $CDCl_3$ δ164 5 (NC triplet, J(N-C)=6 Hz), δ138 3 (=CH singlet), δ136 3 (arene singlet), δ134 8 (arene singlet), δ129 1 (arene singlet), δ114 7 (=CH triplet, J(N-C) = 12 Hz) , δ20 9 (CH_3 singlet), infrared ν (CN) at 2122 cm $^{-1}$ in CH_2Cl_2, anal calcd for $C_{12}H_{13}N$ C, 84.2, H, 7 6, N, 8 2 Found C, 84 1, H, 7 7, N, 8 1

Preparation of $CH_3CH=C(CH_3)-CH=CHNC$

A procedure analogous to the preparation of $(CH_3)_3CCH=CHNC$ above was followed using in sequence solutions of 10 0 g. (244 mmoles) of methyl isocyanide in 300 ml of tetrahydrofuran, 155 ml (248 mmoles) of 1 6 M n-butyllithium in hexane, 20 0 g (238 mmoles) of $CH_3CH=C(CH_3)-CHO$ (tiglaldehyde) in 100 ml. of tetrahydrofuran, 46 5 g (244 mmoles) of p-toluenesulfonyl chloride in 140 ml of tetrahydrofuran, and 21 3 g. (330 mmoles) of 87% potassium hydroxide in 100 ml of methanol Evaporation of the dried ether extracts in a water aspirator vacuum followed by vacuum distillation of the residue gave 14 46 g. (56% yield) of liquid $CH_3CH=C(CH_3)-CH=CHNC$, proton NMR in $CDCl_3$ δ6 58 (1H, doublet of triplets, J(H-H)= 14 Hz , J(N-H)=2 Hz), δ 5 7 (2H, overlapping multiplets), δ1 76 (3H, doublet, J=8 Hz), δ1 69 (3H, doublet, J=1 Hz), proton-decoupled carbon-13 NMR in $CDCl_3$ δ164 0 (NC broad), δ 141 3 (=CH singlet), δ133 4 (=CH singlet), δ131 2 (=C triplet, J(N-C) = 2 Hz), δ108.0 (=CH triplet, J(N-C)= 13 Hz), δ14 2 (CH_3: singlet), and δ11 5 (CH_3 singlet); infrared spectrum in hexane 2115 (s), 1948 (m), 1642 (m), 1435 (w), 1376 (w), 1010 (w), 944 (m), and 792 (w) cm $^{-1}$

Preparation of cis-$[CH_3CH=C(CH_3)-CH=CHNC]_2Mo(CO)_4$

A solution of 0 70 g (2 33 mmoles) of (nor-C_7H_8)$Mo(CO)_4$ in 50 ml of hexane was treated with 1 514 g (14 1 mmoles) of $CH_3CH=C(CH_3)-CH=CHNC$. The reaction mixture became turbid after stirring for 15 minutes at room temperature Some product precipitated after standing overnight, additional product precipitated upon concentration and cooling to -10°C to give a total of 0 735 g (75% yield) of crude cis$[CH_3CH=C(CH_3)-CH=CHNC]_2Mo(CO)_4$ The analytical sample, dec 84°C, was purified by recrystallization from hexane, proton NMR in $CDCl_3$ δ 6 54 (1H, doublet, J=14 Hz), δ5.81 (1H, doublet, J=14 Hz), δ5.78 (1H, quartet, J=6 Hz), δ 1 75 (3H, doublet, J=6 Hz), and δ1 73 (3H, singlet), proton-decoupled carbon-13 NMR in $CDCl_3$ CO groups not observed, δ164 (NC), δ140 0 (=CH), δ132 9 (=CH), δ131 4 (=C), δ109.2 (=CH), δ14 2 (CH_3), and δ11 6 (CH_3), infrared spectrum in hexane ν(CO) bands at 2008 (w), 1953 (m), and 1940 (s) cm $^{-1}$, anal calcd for $C_{18}H_{18}MoN_2O_4$ C, 51 2, H, 4 3, N, 6 6 Found C, 51 4, H, 4 3, N, 6 6

Preparation of $(CH_3)_2C=CHNC$

(a) $CH_2=C(CH_3)CH_2NHCHO$ A mixture of 20 47 g (288 mmoles) of $CH_2=C(CH_3)CH_2NH_2$ and 24 26g. (327 mmoles) of ethyl formate was boiled under reflux for 5 hr Excess ethyl formate and the ethanol product were removed by distillation at atmospheric pressure Vaccum distillation of the residue gave 25.24 g. (88% yield) of $CH_2=C(CH_3)CH_2NHCHO$, b p 84-85°C/1 0 mm., identified by its proton NMR spectrum

(b) $CH_2=C(CH_3)CH_2NC$ A 500 ml flask fitted with a dropping funnel and an outlet to a -78°C trap was charged with a mixture of 93 0 g (488 mmoles) of p-toluenesulfonyl chloride and 180 g (1,390 mmoles) of quinoline The dropping funnel was charged with 36 1 g (364) mmoles) of $CH_2=C(CH_3)CH_2NHCHO$. After evacuating the system in a water aspirator vacuum (~25 mm), the methallylformamide was dropped into the p-$CH_3C_6H_4SO_2Cl$/quinoline so that the effluent vapors were condensed into the -78° C trap Redistillation of the liquid collected in the -78°C trap at atmospheric pressure gave 16 8 g (57% yield) of $CH_2=C(CH_3)CH_2NC$, b p 128-130°C, proton NMR (neat liquid) δ 5 11 (1H, singlet), δ 5 00 (1H, singlet), δ3 96 (2H, singlet) and δ1 80 (3H, singlet), proton-decoupled carbon-13 NMR, δ157.7 (NC triplet, J(N-C)=6 Hz), δ136 4 (=C singlet), δ113 7 (CH singlet), δ 47 9 (CH_2 triplet, J(N-C)=7 Hz), and δ 19 8 (CH_3 singlet), infrared spectrum ν(CN) at 2080 cm $^{-1}$ and ν(C=C) at 1630 cm $^{-1}$

(c) $(CH_3)_2C=CHNC$ Pure $CH_2=C(CH_3)CH_2NC$ (16 8 g , 207 mmoles) is treated with 0 292 g (2 04 mmoles) of copper (I) oxide with stirring After a few seconds the mixture became dark and effervesced. After stirring for 4 hours, the mixture was distilled at atmospheric pressure to give 13 6 g (81% yield) of $(CH_3)_2C=CHNC$, b p 118-120°C, proton NMR in $CDCl_3$ δ5 60 (1H, singlet), δ 1 90 (3H, singlet), and δ 1 78 (3H, singlet), proton-decoupled carbon-13 NMR in $CDCl_3$ δ162 6(NC triplet, J(N-C)=6 Hz), δ 142 5 (=C singlet), δ107 7 (=CH triplet, J(N-C)=12 Hz), δ 21 1(CH_3 singlet), and δ18 5 (CH_3 singlet), infrared spectrum in hexane ν(CN) at 2125 cm $^{-1}$ and ν(C=C) at 1600 cm $^{-1}$

Preparation of cis-$[(CH_3)_2C=CHNC]_2Mo(CO)_4$

A solution of 0 70 g (2 33 mmoles) of (nor-C_7H_8)$Mo(CO)_4$ in 50 ml of hexane was treated with 1 266 g. (15 6 mmoles) of $(CH_3)_2C=CHNC$ After stirring at room temperature for 3 days, the reaction mixture was filtered The filtrate was concentrated and then cooled overnight at -10°C to precipitate 0 777 g. (90% yield) of yellow cis-$[(CH_3)_2C=CHNC]_2Mo(CO)_4$, m p 45-46°C, proton NMR in $CDCl_3$ δ5 57 (1H, singlet), δ 1 87 (3H, singlet), and δ 1 77 (3H, singlet), carbon-13 NMR in $CDCl_3$ δ 210 0 (CO), δ 206 0 (CO), δ163 9 (NC), δ142 2 (=C), δ109 1 (=CH), δ21 4(CH_3), and δ 18 8 (CH_3), infrared spectrum in hexane ν(CN) at 2140 (w) and 2124 (w) cm $^{-1}$, ν(CO) at 2008 (s), 1950 (vs), and 1940 (vs) cm.$^{-1}$, anal calcd for $C_{14}H_{14}MoN_2O_4$ C, 45 4, H, 3 8, N, 7 6 Found C, 45 5, H, 3 8, N, 7 6

Preparation of $CH_3CH=C(CH_3)NC$

A sample of 14.8 g (208 mmoles) of $CH_2=CHCH(CH_3)NH_2$, prepared from 3-chloro-1-butene by the Gabriel procedure[13], was converted to $CH_3CH=C(CH_3)NC$ by a procedure essentially identical to the conversion of $CH_2=C(CH_3)CH_2NH_2$ to $(CH_3)_2=CCHNC$ described above. The products at each of the stages of this synthesis had the following properties

(a) $CH_2=CHCH(CH_3)NHCHO$ 70% yield, b p 75-77°C/1 0 mm , proton NMR δ8.07 (1H, singlet), δ5.7 (1H, broad), δ5 2 (2H, multiplet), δ 4 6 (1H, broad), δ3 15 (1H, singlet), and δ1 27 (3H, doublet, J=7 Hz)

(b) $CH_2{=}CHCH(CH_3)NC$ 88% yield, b p 121-123°C, proton NMR δ5 62 (1H, broad), δ 5 58 (1H, doublet ?), δ5 19 (1H, doublet, J=10 Hz), δ4 23 (1H, broad), and δ1 46 (3H, doublet of triplets, J_D=7 Hz , J_T = 2 Hz), proton-decoupled carbon-13 NMR in $CDCl_3$ δ155 8 (NC triplet, J(N-C)=5 Hz), δ134 3(=CH_2 singlet), δ115 1 (=CH singlet), δ51 4 (CH triplet) J(N-C)=6 Hz), and δ21 7 (CH_3 singlet), infrared spectrum in hexane ν(CN) at 2133 cm^{-1} and ν(C=C) at 1644 cm^{-1}

(c) $CH_3CH{=}C(CH_3)NC$ 55% yield, b p 110-112°C, proton NMR δ5 4 (1H, broad), and δ1 7 (6H, multiplet), proton-decoupled carbon-13 NMR in $CDCl_3$ δ164 2 (NC triplet, J(N-C) = 6 Hz), δ125 1 (=CH singlet), δ121 8 (=C triplet, J(N-C)=11 Hz), δ20 6 (CH_3 singlet), and δ13 1 (CH_3 singlet), infrared spectrum in hexane ν(CN) at 2112 cm^{-1} and ν(C=C) at 1665 cm^{-1}

RESULTS AND DISCUSSION

The Schöllkopf/Stafforst/Jentsch synthesis of vinyl isocyanides[5] is a "one-pot" synthesis from methyl isocyanide and carbonyl compounds based on the following sequence of reactions

$$CH_3NC + n\text{-}C_4H_9Li \longrightarrow LiCH_2NC + n\text{-}C_4H_{10} \qquad (1a)$$

$$LiCH_2NC + RR'C{=}O \longrightarrow RR'C(OLi)CH_2NC \qquad (1b)$$

$$RR'C(OLi)CH_2NC + TsCl \longrightarrow RR'C(OTs)CH_2NC + LiCl \qquad (1c)$$

$$RR'C(OTs)CH_2NC + KOH \longrightarrow RR'C{=}CHNC + KOTs + H_2O \qquad (1d)$$

(Ts = p-toluenesulfonyl)

Until the tosylation reaction (equation 1c) is complete, the temperature of the reaction mixture must be kept low (Dry ice bath) first in order to prevent decomposition of the lithium derivative $LiCH_2NC$ formed in step 1a and subsequently to prevent cyclization of the $RR'C(OLi)CH_2NC$ formed in step 1b to a 2-oxazoline derivative[15] A major difficulty in the application of this synthetic method to the preparation of relatively volatile vinyl isocyanides is the need to separate relatively small quantities of product from the relatively large quantities of solvents (tetrahydrofuran, hexane, and methanol) present in the reaction mixture by the time step 1d is completed This, of course, is not a problem in the preparation of the solid 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$, which crystallizes directly from the diethyl ether extracts of the crude reaction mixture The Schöllkopf/Stafforst/Jentsch synthesis can be used to synthesize the tert-butylvinyl derivative $(CH_3)_3CCH{=}CHNC$ in relatively good yield from pivalaldehyde, although close attention is needed during the distillation procedure not to lose this relatively volatile isocyanide among the reaction solvents This method for the synthesis of $(CH_3)_3CCH{=}CHNC$ is more convenient than the reported[7] synthesis of this isocyanide from $(C_2H_5O)_2P(O)CHLiNC$ and pivalaldehyde More interestingly, the Schöllkopf/Stafforst/Jentsch method can be used to convert the unsaturated tiglaldehyde, $CH_3CH{=}C(CH_3)CHO$, into the 1,3-dienyl isocyanide, $CH_3CH{=}C(CH_3){-}CH{=}CHNC$, apparently the first example of a 1,3-dienyl isocyanide

The Saegusa/Murase/Ito synthesis of vinyl isocyanides[6] is a multistep synthesis from allylic primary amines based on the following sequence of reactions

$$RR'C{=}CR''{-}CHR^3NH_2 + EtOCHO \longrightarrow RR'C{=}CR''{-}CHR^3NHCHO + EtOH \qquad (2a)$$

$$RR'C{=}CR''{-}CHR^3NHCHO + TsCl + C_9H_7N \longrightarrow RR'C{=}CR''{-}CHR^3NC + [C_9H_8N]OTs + [C_9H_8N]Cl \qquad (2b)$$

(C_9H_7N=quinoline)

$$RR'C{=}CR''{-}CHR^3NC \xrightarrow{Cu_2O} RR'CHC(R''){=}C(R^3)NC \qquad (2c)$$

The allylformamide and allyl isocyanide intermediates from steps 2a and 2b, respectively, are both purified by distillation before proceeding to the next step and the final step (2c) is conducted in the absence of a solvent Therefore, the problem of separating a volatile isocyanide from a solvent is avoided so that this method is particularly well suited for the preparation of low molecular weight vinyl isocyanides Saegusa, Murase, and Ito[6] have used this method for the preparation of propenyl isocyanide, $CH_3CH{=}CHNC$, from allylamine, $CH_2{=}CHCH_2NH_2$ (i e , $R{=}R'{=}R''{=}R^3{=}H$) and we report in this paper the extension of this method to the preparations of $(CH_3)_2C{=}CHNC$ ($R{=}R'{=}R^3{=}H$, $R''{=}CH_3$) and $CH_3CH{=}C(CH_3)NC$ ($R{=}R'{=}R''{=}H$, $R^3{=}CH_3$)

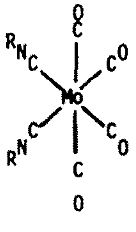
Spectroscopic methods played a major role in the characterization of the vinyl isocyanides obtained from this project Their carbon-13 NMR spectra were most indicative since in general the resonances from all of the carbon atoms could be identified The isocyanide carbon and the vinyl carbon bearing the isocyanide group were recognized in the carbon-13 NMR spectrum by their appearance as 1 1 1 triplets, owing to the $^1J(C-N)$ coupling with the spin 1 nitrogen-14 atom of the isocyanide group Isocyanides are one of the few types of nitrogen compounds in which the electric field gradient around the nitrogen atom is sufficiently small so that spin-spin splitting is observed from the quadrupolar nitrogen-14 to neighboring nuclei[16] The isocyanide carbons appeared in the range δ162-165 with a $^1J(C-N)$ of 6 Hz. whereas the vinylic carbons bearing the isocyanide group appeared in the range δ 107-122 with $^1J(C-N)$ in the range 11-13 Hz for the five new vinyl isocyanides reported in this paper The carbon-13 chemical shift range in the new compounds for the vinylic carbons <u>not</u> bearing the isocyanide group was significantly larger, i e from δ149.2 in $(CH_3)_3CCH=CHNC$ to δ 125 1 in $CH_3CH=C(CH_3)NC$ Our observations on the carbon-13 NMR spectra of these vinyl isocyanides are consistent with earlier reports [17,18]

The proton NMR spectra of vinyl isocyanides of the type RCH=CHNC exhibited the expected AB pattern for the vinyl resonances with J(A-B) in the range of 14-15 Hz In some cases further 1 1 1 splitting was observed apparently arising from J(N-H) coupling The infrared spectra of the new vinyl isocyanides exhibited a relatively strong ν(CN) frequency at 2110-2125 $cm.^{-1}$ from the isocyanide group and a relatively weak ν(C=C) frequency at 1600-1655 cm^{-1}

An analytical sample of the solid $2,4,6-(CH_3)_3C_6H_2CH=CHNC$ was readily obtained by recrystallization, vacuum sublimation could also be used to purify this compound but with more extensive losses owing to some thermal decomposition The remaining new isocyanides are liquids, which were converted to crystalline $cis-(RNC)_2Mo(CO)_4$ derivatives by reaction with the norbornadiene complex according to the following scheme[19]

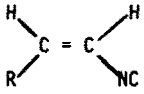
$$2RNC + C_7H_8M(CO)_4 \longrightarrow cis\text{-}(RNC)_2Mo(CO)_4 + C_7H_8 \qquad (3)$$

These molybdenum carbonyl complexes gave excellent elemental analyses (C, H, and N) for the indicated formulas Their $cis-L_2Mo(CO)_4$ stereochemistry was indicated by their ν(CO) frequencies[20] which also are close to the reported[19] values for $cis-[(CH_3)_3CNC]_2Mo(CO)_4$ The proton and carbon-13 NMR spectra of the $cis-(RNC)_2Mo(CO)_4$ complexes derived from vinyl isocyanides indicated that the carbon-carbon double bonds are not bonded to the molybdenum atom No examples of 1 1 1 splitting arising from nitrogen-14 coupling were observed in the proton or carbon-13 NMR spectra of the vinyl isocyanide molybdenum carbonyl complexes in accord with the expected substantial increase in the electric field gradient around the nitrogen atom upon complexation with molybdenum[16] All of these spectroscopic observations indicate structure I ($R=(CH_3)_3CCH=CH$, $CH_3CH=C(CH_3)-CH=CH$, and $(CH_3)_2C=CH$) for the new $cis-(RNC)_2Mo(CO)_4$ complexes reported in this paper

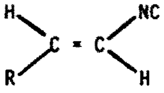


I

Vinyl isocyanides of the type RCH=CHNC can exist as the cis (IIa) and trans (IIb) isomers.



IIa



IIb

In this connection the carbon-13 NMR spectra of the new vinyl isocyanides $(CH_3)_3CCH=CHNC$ and $CH_3CH=C(CH_3)-CH=CHNC$ exhibit a second weak =CHNC vinylic carbon resonance in addition to the relatively strong 1 1 1 triplet reported in the Experimental Section This suggests that these vinyl isocyanides are predominantly one of the two stereoisomers IIa or IIb but that the second stereoisomer is present in relatively small quantity This observation prompted a closer examination of this region of the carbon-13 NMR spectrum for all five vinyl isocyanides of the type RCH=CHNC that were available to us including the two known compounds $C_6H_5CH{=}CHNC$ and $CH_3CH{=}CHNC$ which were prepared as reported by the Schöllkopf/Stafforst/Jentsch[5] and Saegusa/Murase/Ito[6] methods, respectively The results are summarized in Table 1 Interestingly enough, the styryl derivative $C_6H_5CH{=}CHNC$ contained significant amounts of both stereoisomers whereas the propenyl derivative $CH_3CH{=}CHNC$ appeared to consist of a single stereoisomer This suggests that the Saegusa/Murase/Ito method for preparing vinyl isocyanides by copper(I) catalyzed isomerization[6] is more stereospecific than the Schöllkopf/Stafforst/ Jentsch[5] method for preparing vinyl isocyanides by an elimination reaction The isolation of a single stereoisomer of the mesitylvinyl derivative $2,4,6\text{-}(CH_3)_3C_6H_2CH{=}CHNC$ as compared with the isolation of a mixture of stereoisomers of the styryl derivative $C_6H_5CH{=}CHNC$ using the same preparative method in both cases may relate to the solid nature of the mesitylvinyl derivative which allows separation of a pure stereoisomer by crystallization Also formation of vinyl isocyanides of the type RCH=CHNC having relatively bulky R substituents (e g , R = tert-butyl or mesityl) by the Schöllkopf/ Stafforst/Jentsch method[5] may be more nearly stereospecific for steric reasons than the formation of such vinyl isocyanides having less bulky R substituents such as phenyl Obviously, many more examples of such observations on RCH=CHNC derivatives are needed before definite conclusions can be drawn

TABLE 1

CIS-TRANS ISOMER RATIOS IN RCH=CHNC DERIVATIVES

Vinyl Isocyanide R group	Equations of Preparative Method	=CHNC Vinyl Carbon Atom		
		Isomer Ratio	Carbon-13 Chemical Shift Values	$^1J(^{13}C\text{-}^{14}N)$ Hz
CH_3	2a-2c	100/0	113 0/-	12/-
$(CH_3)_3C$	1a-1d	15/85	112 5/109 5	-/13
$CH_3CH{=}C(CH_3)$	1a-1d	10/90	110 3/108 0	-/13
C_6H_5	1a-1d	40/60	110 8/108 8	13/12
$2,4,6\text{-}(CH_3)_3C_6H_2$	1a-1d	100/0	113 0/-	12/-

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