stretch), 8.2 (s) (CF), 8.75 (w), 9.62 (s), 10.03 (m), 11.59 (m), 11.91 (m), 12.30 (s), 12.78 (m), 13.7 (w), and 14.1 (w).

B. From Difluoronitroacetonitrile.—Difluoronitroacetonitrile (0.02 mole) and ammonia (0.01 mole) were condensed into an evacuated 150-ml. Pyrex bulb. The bulb then was placed in an ice bath for 18–24 hr. Volatiles were removed on the vacuum manifold, and the liquid product was distilled as before to yield 2.34 g. (86%) of IIa. Its infrared spectrum was identical with that of material prepared from the amidine. If ratios of nitrile to ammonia of greater than two to one were employed, only two equivalents of nitrile were consumed; the remainder could be recovered quantitatively.

Copper Chelate of IIa.—IIa (0.20 g., 1.25 mmole) dissolved in 0.5 ml. of 1,2-dimethoxyethane was shaken with a solution of 0.15 g. (0.66 mmole) of cupric nitrate trihydrate in 1.0 ml. of water. The precipitated, rust-colored solid was removed by centrifugation, washed twice with 0.5-ml. portions of water, and dried at room temperature and 5 μ for 5 hr.; weight 0.17 g. (48%). After one recrystallization from benzene containing a few drops of 95% ethanol, it melted above 200°. It was very soluble in 95% ethanol, forming dark maroon solutions.

N-Methyl- and N,N-Dimethyl-N′-(difluoronitroacetylimino)-difluoronitroacetamidine (IIb and IIc).—IIb and IIc were prepared by method B. Major infrared absorption bands for IIb were at 2.97 (m) (NH stretch), 3.20 (w), 3.45 (w) (CH stretch), 5.93 (s) (NC=N asym. stretch), 6.03 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.55 (m), 6.90 (w), 7.09 (w), 7.40 (m) (NO_2 sym. stretch), 7.65 (w), 8.25 (s) (CF), 8.83 (w), 9.38 (m), 9.80 (m), 10.20 (m), 11.60 (w), 11.90 (m), 12.00 (w), 12.20 (m), 12.35 (m), 12.80 (m), 13.1 (w), and 13.8 (w). For IIc they were at 3.00 (w) (=NH stretch), 3.47 (m) (CH stretch), 6.20 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.70 (m), 7.08 (m), 7.48 (m) (NO_2 sym. stretch), 8.00 (s), 8.20 (s) (CF), 8.45 (w), 8.65 (m), 9.70 (m), 10.20 (m), 11.63 (m), 11.83 (m), 12.03 (w), 12.17 (m), 12.40 (m), and 12.80 (m).

N-Phenyl-N′-(difluoronitroacetylimino)difluoronitroacetamidine (IId).—The phenyl compound was prepared by method B except that the amine was measured into the reactor and was frozen in liquid nitrogen prior to evacuation, and the 0° reaction period was followed by an additional 24 hr. at room temperature. Major infrared absorption bands were at 3.00 (w) (=NH stretch), 6.00 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.80 (m), 7.20 (w), 7.45 (m) (NO_2 sym. stretch), 8.15 (s) (CF), 8.40 (m), 9.40 (w), 9.78 (w), 11.00 (w), 11.90 (m), 12.10 (m), 12.85 (w), 13.2 (w), 13.7 (w), and 14.4 (m).

Difluoronitromethane.—Difluoronitroacetamidine (0.40 g., 2.91 mmoles) was heated for 3 hr. at 95–105° under 400 mm. of helium. Difluoronitromethane (1.77 mmoles, 61%) was collected in a liquid nitrogen-cooled trap atop a short air condenser. Major infrared absorption bands for the vapor were at 3.30 (w), 3.40 (w) (CH stretch), 3.70 (vw), 4.36 (vw), 6.22 (s) (NO_2 asym. stretch), 7.38 (m) (NO_2 sym. stretch), 7.60 (m), 8.55 (s), 10.70 (m), and 12.5 (m). Approximately 50% yields could be obtained by similar thermal decomposition of IIa or IIb. The molecular weight as determined by PVT measurements was 96.4 (calcd. 97.0).

3-Difluoronitromethyl-1,2,4-triazole (IIIa).—IIa (1.68 g., 6.44 mmoles) was heated at 120° for 3 hr. under 400 mm. of helium. The difluoronitromethane which was evolved was collected in a liquid nitrogen-cooled trap atop a short air condenser and amounted to 5.24 mmoles. Heating for an additional 24 hr. at 100–110° under 400 mm. of helium resulted in evolution of an additional 0.21 mmole of difluoronitromethane. Heating the residue at 100–110° at 1 μ caused sublimation of 0.53 g. (50%) of crystalline triazole melting at 73.5–76°. After two recrystallizations from benzene–petroleum ether, it melted at 76–77° (unchanged by sublimation at 100° and 1 μ). The yield was essentially the same if the triazole was prepared directly from difluoronitroacetonitrile without isolation of the intermediate IIa. Major infrared absorption bands (KBr pellet) were at 2.90 (s) (NH stretch), 2.95 (s) (NH stretch), 3.08 (s) (NH stretch), 3.10 (sh), 3.40 (vw) (CH stretch), 3.70 (vw) (NH ammonium type band), 4.10 (vw), 6.03 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.55 (s), 7.00 (w), 7.14 (w), 7.37 (m) (NO_2 sym. stretch), 8.20 (vs) (CF), 9.33 (m), 9.52 (m), 9.70 (m), 10.18 (s), 10.62 (m), 11.59 (m), 11.99 (m), 12.13 (s), 12.78 (s), 13.22 (w), 13.80 (w), and 14.7 (w).

3-Difluoronitromethyl-2(or 4)-methyl-1,2,4-triazole(IIIb).—Difluoronitroacetonitrile (0.02 mole) and methylamine (0.01 mole) were condensed into a 60-ml. evacuated Pyrex bulb. After 20 hr. at 0° the bulb was filled to a pressure of 400 mm. with helium and heated at 100–110° for 7 hr. Difluoronitromethane (5 mmoles, 25% based on nitrile) evolved during the heating was collected in a liquid nitrogen-cooled trap. The liquid remaining in the reaction bulb was distilled at 130–140° and 2–5 μ to yield 1.20 g. (33%) of light yellow liquid. Major infrared absorption bands were at 2.90 (m) (NH stretch), 3.40 (CH stretch), 5.95 (sh) (NC=N asym. stretch), 6.15 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.55 (m), 6.90 (w), 7.09 (m), 7.41 (m) (NO_2 sym. stretch), 8.10 (s) (CF), 8.85 (w), 9.70 (w), 10.20 (m), 11.60 (w), 12.00 (w), 12.20 (m), and 12.80 (m).

Acknowledgment.—The author is indebted to Robert Lim and Elinor R. Smathers for the microchemical analyses and to Douglas B. Fields for preparation of part of the difluoronitroacetonitrile and for obtaining some of the infrared spectra. James A. Happe provided the nuclear magnetic resonance data.

Addition Compounds of Thiols and 1-Substituted Nicotinamides[1,2]

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van Eys and Kaplan have observed that "the ubiquitous nature of sulfhydryl compounds in biological systems" makes the addition reactions of thiols and diphosphopyridinenucleotide[5] (DPN) and its analogs of "particular interest."[6] The addition of a sulfhydryl enzyme to the 4-position of DPN has been suggested as an intermediate in the oxidation of aldehydes catalyzed by glyceraldehyde-3-phosphate dehydrogenase.[7]

Evidence for the addition of sulfide ion and of thiols to DPN has been adduced from changes in ultraviolet spectra.[6,8]

Wallenfels and Schüly have reported the synthesis of addition compounds of nicotinamide-1-(2,6-dichlorobenzylo) bromide and sulfide ion, benzyl mercaptan, 2-mercaptothiazole, β-phenylethyl mercaptan, ethyl mercaptan, thiocyanate ion, and thiophenol.[9]

In connection with investigations of some model systems for enzymic oxidation and reductions, new adducts of L-cysteine ethyl ester, ethyl thioglycolate, and *n*-propyl mercaptan with nicotinamide-1-(2,6-dichlorobenzylo) bromide have been prepared by addition of the mercaptan in aqueous sodium hydroxide to an aqueous solution of the quaternary bromide. These addition compounds were isolated as crystalline solids and their infrared and ultraviolet spectra were similar to each other.

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(2) Taken from J. M. Kolyer, Ph.D. thesis, University of Pennsylvania, 1960.

(3) Department of Chemistry, Syracuse University, Syracuse, N. Y.

(4) Walter T. Taggart Memorial Fellow, 1959–1960.

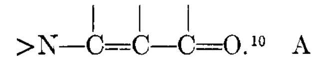
(5) Nicotinamide–adenine–dinucleotide.

(6) J. van Eys and N. O. Kaplan, *J. Biol. Chem.*, **228**, 305 (1957).

(7) I. Krimsky and E. Racker, *Science*, **122**, 319 (1955).

(8) H. Terayama and C. S. Vestling, *Biochem. Biophys. Acta*, **20**, 586 (1956); J. van Eys, N. O. Kaplan, and F. E. Stolzenbach, *ibid.*, **23**, 221 (1957).

(9) (a) K. Wallenfels and H. Schüly, *Ann.*, **621**, 86 (1959); (b) K. Wallenfels and H. Schüly, *Angew. Chem.*, **69**, 505 (1957).

The infrared spectra (taken in potassium bromide disks) of these addition compounds of thiols have very strong characteristic absorption at about 1560 cm.$^{-1}$, an absorption which has been attributed to a vinylogous amide group:  $>N{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O$.[10] Absorption at 1560 cm.$^{-1}$ occurs in 1,4-dihydronicotinamides and also in a compound alleged to be a 1,6-dihydronicotinamide derivative which was obtained by the reduction of nicotinamide-1-(2,6-dichlorobenzylo)bromide with sodium borohydride.[11] The absorption at 1560 cm.$^{-1}$ is much less intense or is absent in typical 1-substituted nicotinamide salts. The infrared spectrum of the addition compound of *n*-propanethiol also differs considerably in other absorption regions from the combined spectra of nicotinamide-1-(2,6-dichlorobenzylo)-chloride and *n*-propanethiol. The infrared spectrum of the mercaptide salt (where the mercaptide ion replaces halide ion) might, to a first approximation, be expected to be the sum of the spectra of nicotinamide-1-(2,6-dichlorobenzylo)chloride and of *n*-propanethiol minus the –SH absorption.

There are points of similarity in the infrared spectra of the adducts and the spectra of both the 1,4- and 1,6-dihydronicotinamides, and it does not seem possible to assign the structure on the basis of these spectra.[12] Some typical spectra are given in the Experimental section.

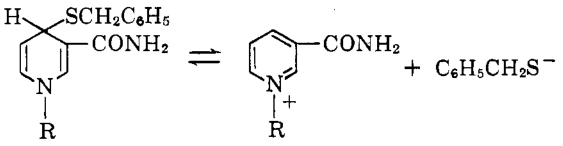
The 1,6-dihydronicotinamide was reported to have maxima in the ultraviolet spectrum at 265 (ϵ 9840) and 355 mμ (ϵ 7450) in methanol, the two maxima being attributed to cross conjugation in excited states.[11] The adducts of thiols and 1-substituted nicotinamides reported previously had one or two maxima in the ultraviolet depending on the solvent or on the concentration; the extinction coefficient for absorption at lower wave length was always greatest.[9a] The lower wave length band was believed to be caused by the dissociation of the addition compounds into the thiolate anion and the quaternary pyridinium ion. The benzyl mercaptan adduct had absorption at 333 mμ in benzene,[2] at 330 mμ in dioxane,[9a] at 316 and 254 mμ in ethanol,[9a] and at 265 mμ in water.[9a] The presence of only one absorption band at 330 mμ in the nonpolar solvents (where dissociation is minimized) may be considered as indicating a 1,4- rather than a 1,6-dihydro structure for the addition compounds; the 1,4-dihydro structure may be preferred on steric grounds.

In solution the addition compounds may exist as charge transfer complexes since the long wave length maximum for the benzyl mercaptan adduct increased from 315 mμ to 330 mμ on going from methanol to dioxane or benzene. However, the ultraviolet maximum for the addition compound of benzyl mercaptan does not shift to longer wave lengths as the polarity of the medium is decreased by changing the solvent from water to ethanol (see Table I). A shift to longer wave lengths as the polarity of the medium is decreased has been suggested as diagnostic of a charge-transfer complex.[13]

The addition compounds are colorless or nearly so. Crude material is generally bright yellow, but the intensity of the color decreases with repeated crystallizations. The original yellow color may be an impurity from the reaction of the nicotinamide salt with hydroxide ion.[14] The addition compound of cyanide ion and nicotinamide-1-(2,6-dichlorobenzylo)bromide is nearly colorless.[9a]

The 1,4-dihydropyridine structure, therefore, is unproved but is analogous to the structures proposed for the addition of cyanide and other substances to 1-substituted nicotinamides.[15] The rather wide melting point of the L-cysteine ethyl ester derivative may indicate that the material obtained is a mixture of position isomers or of mercaptide salt and addition compound.

The adducts are dissociated readily in polar media analogous to the dissociation of cyanide adducts.[16]



I

R = 2,6-dichlorobenzyl

Treatment of addition compound I with hydrogen chloride in chloroform gave the quaternary chloride salt. Treatment of I with a dilute solution of malachite green oxalate in chloroform caused immediate decolorization of the dye. The same behavior was observed in ethanol from which was isolated the addition compound of benzyl mercaptan and malachite green cation. In an analogous reaction, cyanide adducts similar to I transfer cyanide ion to malachite green.[9a]

Experimental

Nicotinamide-1-(2,6-dichlorobenzylo)-bromide.—A mixture of N-bromosuccinimide (10.0 g., 0.056 mole) and 2,6-dichlorotoluene (Aldrich Chemical Co.) (9.0 g., 0.056 mole) in 40 ml. of carbon tetrachloride was refluxed for 31 hr. The solid was removed and the filtrate was fractionally distilled to remove the carbon tetrachloride. Nicotinamide (6.1 g. 0.050 mole) and 25 ml. of absolute alcohol were added, and the solution was refluxed for 12 hr. When the reaction mixture was chilled, the product separated as tan crystals (9.9 g., 48%) and was recrystallized from ethanol–water to give fine white crystals, m.p. 248–249° (lit.[9b] m.p. 245–246°).

Preparation of Thiol Addition Compounds. 1. L-Cysteine Ethyl Ester Adduct.—Nicotinamide-1-(2,6-dichlorobenzylo)-bromide (0.364 g., 0.00101 mole) and L-cysteine ethyl ester hydrochloride (Mann Research Laboratories) (1.99 g., 0.0107 mole) were dissolved in 10 ml. of distilled water. The solution was chilled in an ice bath and stirred while 10% sodium hydroxide solution was added from a buret. After 7.1 ml. had been added, the precipitate did not redissolve on stirring. An additional 0.5 ml. of base was added, and the mixture was stirred briefly.

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[10] A. G. Anderson, Jr., and G. Berkelhammer, *J. Am. Chem. Soc.*, **80**, 992 (1958).

[11] K. Wallenfels and H. Schüly, *Ann.*, **621**, 106 (1959). [Sodium borohydride reduces the 1-phenylpyridinium ion to 1-phenyl-1,2-dihydropyridine whose structure was proved by proton n.m.r. spectroscopy. M. Saunders and E. H. Gold, *J. Org. Chem.*, **27**, 1439 (1962).]

[12] We wish to thank a referee for suggesting that the infrared spectra might help in establishing a structure.

[13] E. M. Kosower in P. D. Boyer, H. Lardy, and K. Myrbäck, "The Enzymes," Vol. 3, 2nd Ed., Academic Press, New York, N.Y., 1960, p. 183.

[14] A. G. Anderson, Jr., and G. Berkelhammer, *J. Org. Chem.*, **23**, 1109 (1958).

[15] A. San Pietro, *J. Biol. Chem.*, **217**, 579 (1955); M. B. Yarmolinsky and S. P. Colowick, *Biochim. Biophys. Acta*, **20**, 177 (1956); R. M. Burton and N. O. Kaplan, *J. Biol. Chem.*, **206**, 283 (1954); R. M. Burton and N. O. Kaplan, *ibid.*, **211**, 447 (1954).

[16] M. R. Lanborg, R. M. Burton, and N. O. Kaplan, *J. Am. Chem. Soc.*, **79**, 6173 (1957); K. Wallenfels and H. Diekmann, *Ann.*, **621**, 166 (1959).

Filtration gave a white powder (0.033 g., 8%), m.p. 93–102° dec., which was dried over phosphorus pentoxide under reduced pressure; λ_{max} (ethanol) 255 (ϵ 4.9 × 10^3), 315 mμ (ϵ 3.9 × 10^3), λ_{max} (50% ethanol) 268 mμ (ϵ 5.2 × 10^3).

Anal. Calcd. for $C_{18}H_{21}N_3O_3SCl_2$: C, 50.23; H, 4.92; N, 9.76. Found: C, 50.51; H, 4.77; N, 10.11.

When this compound was chromatographed on Whatman no. 1 paper (solvent, 4:1:5 butanol–acetic acid–water) and the chromatogram developed with fresh 1% sodium nitroprusside in 0.05 *N* sodium hydroxide solution both cysteine ethyl ester and cysteine were identified.

2. **Ethyl Thioglycolate Adduct.**—Ethyl thioglycolate (2.6 g., 0.022 mole) in 20 ml. of 5% sodium hydroxide solution was added to nicotinamide-1-(2,6-dichlorobenzylo)-bromide (1.01 g., 0.00279 mole) in 20 ml. of distilled water. After 10 min. the product (0.96 g., 86%) was removed by filtration, washed with water and dried. Recrystallization from ethanol–benzene gave nearly white crystals, m.p. 131–132°; λ_{max} (ethanol) 255 (ϵ 4.1 × 10^3), 316 mμ (ϵ 2.4 × 10^3); λ_{max} (50% ethanol) 267 mμ (ϵ 3.1 × 10^3).

Anal. Calcd. for $C_{17}H_{18}N_2O_3SCl_2$: C, 50.88; H, 4.52; N, 6.98. Found: C, 50.56, 50.64; H, 4.55, 4.67; N, 6.83, 6.87.

When this adduct was chromatographed on paper as described previously, ethyl thioglycolate was identified.

3. ***n*-Propyl Mercaptan Adduct.**—This addition compound was prepared from *n*-propyl mercaptan in the same way as the adduct of ethyl thioglycolate. The crude yellow product was recrystallized from cold ethanol to give a white powder, m.p. 96–98°, λ_{max} (ethanol) 256 (ϵ 4.3 × 10^3), 316 mμ (ϵ 2.7 × 10^3).

Anal. Calcd. for $C_{16}H_{18}N_2OSCl_2$: C, 53.78; H, 5.08. Found: C, 53.91, 54.03; H, 5.13, 5.27.

Ultraviolet Spectra of Benzyl Mercaptan Adduct in Ethanol–Water Mixtures.—The benzyl mercaptan adduct, m.p. 131–132° (lit.[9a] m.p. 131–133°), was prepared by the same method as the ethyl thioglycolate adduct. The effect of the polarity of the medium on the ultraviolet spectrum of this adduct are summarized in Table I.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF BENZYL MERCAPTAN ADDUCT IN ETHANOL–WATER SOLUTIONS

Water, ml.	Ethanol, ml.	Concn. × 10^4 *M*	λ_{max}, mμ	ϵ × 10^{-3}	λ_{max}, mμ	ϵ × 10^{-3}
0	50	1.0	316	4.8	254	7.1
5	45	1.1	315	2.4	257	4.5
10	40	1.5	317	1.6	257	3.9
20	30	1.1	317	0.45	265	3.6
30	20	1.4	317	.14	265	3.8
40	10	0.99	317	.09	265	6.7

Reaction of Benzyl Mercaptan Adduct with Hydrogen Chloride.—The addition compound (*ca.* 0.1 g.) was dissolved in 10 ml. of chloroform, and anhydrous hydrogen chloride was passed through the solution. The white precipitate, m.p. 235° dec., was shown to be nicotinamide-1-(2,6-dichlorobenzylo)-chloride by a mixture m.p. (236°) and by identity of the infrared spectra. Nicotinamide-1-(2,6-dichlorobenzylo)-chloride was prepared by heating a mixture of 2,6-dichlorotoluene (16.1 g., 0.100 mole), sulfuryl chloride (6.8 g., 0.050 mole), and benzoyl peroxide (0.2 g., 0.0008 mole) on the steam bath until gas evolution ceased (1 hour). Nicotinamide (6.1 g., 0.050 mole) and 25 ml. of absolute alcohol were added, and the solution was refluxed for 3 hr. When the reaction mixture was cooled, white crystals (7.8 g., 49%) separated. Two recrystallizations from alcohol-water gave white crystals, m.p. 237–238.5° dec.

Anal. Calcd. for $C_{13}H_{11}N_2OCl_3$: C, 49.16; H, 3.49. Found: C, 48.94, 49.13; H, 3.61, 3.73.

Reaction of the Benzyl Mercaptan Adduct with Malachite Green.—A solution of malachite green oxalate (0.5 g.) in 10 ml. of absolute ethanol was heated gently while the adduct was added, with stirring, until the solution was decolorized (pale green). Filtration gave a pale green solid (0.5 g.) and a green filtrate. The solid was soluble in water and insoluble in alcohol and ether. Two recrystallizations from alcohol–water and decolorization with charcoal gave off-white crystals, m.p. 229–230° dec. Analysis by sodium fusion demonstrated the presence of nitrogen and chlorine and the absence of sulfur. With silver nitrate solution, the compound gave an acid-soluble white precipitate (silver oxalate). It was concluded that the compound was nicotinamide-1-(2,6-dichlorobenzylo)oxalate.

Anal. Calcd. for $C_{28}H_{22}N_4O_6Cl_4$: C, 51.55; H, 3.40. Found: C, 51.54, 51.81; H, 3.45, 3.68.

The green filtrate deposited white fluffy crystals (0.1 g.), m.p. 120–122° dec. This compound was identified as the benzyl sulfide of malachite green by m.m.p. (122°) with an authentic sample. The sulfide was prepared also by the dropwise addition of 6 *N* sodium hydroxide solution to a solution of malachite green oxalate (0.4 g., 0.0004 mole) and benzyl mercaptan (1 ml., 0.009 mole) in 15 ml. of absolute ethanol until the solution was decolorized. A tan solid was removed by filtration, and the filtrate was diluted with 5 ml. of ethanol and allowed to stand for 2 hr. Filtration gave fluffy white crystals (0.08 g., *ca.* 50%), m.p. 121–123° dec. This compound turned green on standing in air.

Anal. Calcd. for $C_{30}H_{32}N_2S$: C, 79.60; H, 7.13. Found: C, 79.51, 79.65; H, 7.07, 7.26.

1-(2,6-Dichlorobenzyl)-1,6-dihydronicotinamide.[11]—Sodium borohydride (0.207 g., 0.00547 mole) was added during 1 min. to a stirred solution of nicotinamide-1-(2,6-dichlorobenzylo)bromide (1.00 g., 0.00276 mole) in 15 ml. of distilled water. The crude product precipitated and was recrystallized by dissolving it in 15 ml. of ethanol, adding 15 ml. of water, and chilling. The bright yellow, fine crystals (0.512 g., 66%), m.p. 161–163° dec. [lit.[11] m.p. >150° (dec.)], were dried over potassium pentoxide. The ultraviolet maxima in ethanol were at 354 mμ (ϵ 4200) and 263 mμ (ϵ 4300) [lit.[11] (methanol) 355 mμ (ϵ 7450), 265 mμ (ϵ 9840)].

Comparisons of Infrared Spectra.—The infrared spectra in cm.$^{-1}$ of the following compounds are given.

n-Propanethiol adduct of nicotinamide-1-(2,6-dichlorobenzylo)-bromide: 3450 m, 3150 m, 2975 m, 1675 s, 1654 s, 1608 m, 1562 s (1590–1535), 1465 w, 1454 m, 1434 m, 1409 m, 1380 m, 1356 m, 1342 m, 1283 m, 1222 m, 1204 m, 1170 m, 1090 m, 1085 m, 1032 w, 957 w, 947 w, 920 w, 875 w, 823 w, 800 w, 776 m, 767 m, 750 m, 737 m, 704 w, 667 w.

1-(2,6-Dichlorobenzyl)-1,4-dihydronicotinamide: 3470–3370 w, 3140 w, 2810 w, 1688 m, 1663–1640 m, 1577 (1610–1540) s, 1435 m, 1380 w, 1360 m, 1338 m, 1300 w, 1280 w, 1207 m, 1161 w, 1085 w, 998 w, 952 w, 867 w, 778 w, 764 w, 713 w.

1-(2,6-Dichlorobenzyl)-1,6-dihydronicotinamide: 3375 m, 3190 m, 2775 w, 1680 m, 1643 s, 1598 s, 1580 s, 1562 s, 1435 s, 1430 s, 1385 s, 1359 m, 1340 w, 1317 m, 1308 w, 1282 m, 1220 m, 1201 m, 1178 w, 1162 w, 1128 w, 1021 w, 979 w, 954 w, 870 w, 777 m, 763 w, 729 w, 707 w.

Nicotinamide-1-(2,6-dichlorobenzylo)chloride: 3500 m, 3380 m, 3290 m, 3080 s (3200–2900), 1688 s, 1617 m, 1578 m, 1563 m, 1497 w, 1466 w, 1447 s, 1411 s, 1390 s, 1366 m, 1320 w, 1275 w, 1202 m, 1185 m, 1133 m, 1118 w, 1088 m, 1027 w, 970 w, 948 w, 895 w, 883 w, 852 w, 834 w, 813 m, 793 w, 778 m, 768 m, 755 m, 708 w, 678 m, 672 m.

n-Propanethiol[17]: 4444 w, 2915 s, 2577 w, 2326 w, 1449 s, 1370 m, 1330 w, 1290 m, 1245 s, 1107 w, 1096 w, 920 m, 901 s, 893 s, 813 s, 790 s, 730 s, 704 m.

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[17] Sadtler Standard Spectra, Midget Ed., Sadtler Research Laboratories, Philadelphia, Pa., no. 328 (1962).

The Conjugate 1:4-Addition of Some Acetylenic Grignard Reagents to Cyclohexylidenemalononitrile

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Recently, in another connection, it was found necessary to devise a synthesis of α-(1-acetylcyclohexyl)isovaleric acid (I). By analogy with the well established addition of alkyl Grignard reagents to carbon–carbon