

Isocyanide derivatives of ferrocene. Preparation, complexation and redox properties *

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(Received April 21st, 1987)

Abstract

Syntheses and properties of 11 isocyanides containing the ferrocene moiety, including 7 chiral compounds, are described. The redox properties and spectroscopic data of some of these isocyanides are discussed together with those of their chromium carbonyl complexes.

Introduction

The strong electron-donating ability of the metallocenes, in particular ferrocene, is well known and widely exploited in organometallic chemistry, e.g. for the stabilization of carbocations [1] or phosphonium ions [2]. On the other hand, isocyanides are not only interesting ligands for transition metals [3–7] but also versatile building blocks in organic chemistry [8–11]. As efficient electron acceptors, they stabilize carbanions [12–14].

With these two aspects in mind we decided to prepare molecules containing both ferrocene and isocyanide groups, and we present here our results on the synthesis, spectroscopic properties, electrochemistry, and complexing behaviour of some members of this new class of compounds [15**].

* Dedicated to the late Prof. Dr. Dieter Marquarding who initiated this chemistry.

** This and other references marked with asterisks indicate notes occurring in the list of references.

Table 1

Synthesis of the formamides **2** and the isocyanides **3** from the amines **1**

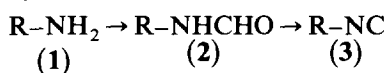
R ^a	2		3		$\nu(\text{NC})$ (cm ⁻¹)	Ref.
	Yield (%)	M.p. (°C)	Yield (%)	M.p. (°C)		
1a Fc	78	88–90	63	73–75	2120 (CCl ₄)	18
1b CH ₂	74 [23]	92–94	58	81–83	2145 (KBr)	19
1c Fc–CH(Me)	74	111–113	67	oil	2140 (film)	20
1d Fc–CH(i-Pr)	71	91–93	78	oil	2140 (film)	20
1e Fc–CH(t-Bu)	80	154–156	85	78–80	2140 (KBr)	20
1f Fc–CH(c-Hex)	87	58–60	77	78–80	2130 (KBr)	20
1g Fc–CH(Men)	82	161–162	90	97–98	2135 (KBr)	21
1h Fc–CH(Pin)	88	198–200	83	113–116	2130 (KBr)	22
1i Fc–CH(Bor)	80	208–210	85	221 (d)	2135 (KBr)	22
1j Fc–CH(CH ₂ OMe)	70	58–59	77	28–29	2140 (KBr)	17
1k Fc–CH=C(CO ₂ Me)	65	125–127	60	99–102	2110 (KBr)	–

^a Abbreviations: Fc = ferrocenyl; CH(Men) = [(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]-(*R*)-methyl; CH(Pin) = {(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]-hept-3-yl}-(*R*)-methyl; CH(Bor) = {(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl}-(*S*)-methyl.

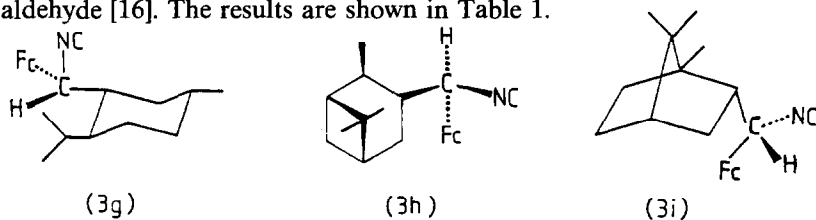
Results and discussion

The most general method for the preparation of isocyanides is the dehydration of *N*-monosubstituted formamides [8]. The sensitivity of ferrocene towards oxidizing agents and acids necessitates the use of particularly mild reagents and reaction conditions. We have found that dehydration with phosphoryl chloride and diisopropylamine [16] is the best method. Attempted syntheses of ferrocenylalkyl isocyanides with trichloromethyl chlorocarbonate (diphosgene)/triethylamine gave a mixture of cyanide and isocyanide and/or ferrocenylalkenes by elimination [16].

The formamides are generally prepared from the corresponding primary amines by reaction with ethyl formate. The process is represented by:



Formamide **2k** is obtained by the reaction of methyl isocyanoacetate with ferrocene aldehyde [16]. The results are shown in Table 1.



Use of the pure enantiomers of the amines **1c–1i** as substrates gave the isocyanides **3** as pure enantiomers. No racemization occurs during the preparation, as is evident from the fact that hydrolysis of the isocyanide regenerates the starting amine **1**. The optical rotations and configurational assignments of the isocyanides are listed in Table 2.

Except for compound **1g**, the sign of the optical rotation of the isocyanide is the same as that of the starting amine, while the formamides show optical rotations of

Table 2
Optical rotations and configurational assignments of the optically active compounds **1**, **2** and **3**

Compounds	Configuration	Optical rotations $[\alpha]_D^{22}$			Ref.
		1 (<i>c</i> = 1, benzene)	2 (<i>c</i> = 1, ethanol)	3 (<i>c</i> = 1, ethanol)	
1c	(<i>R</i>)	-26.3	+40.3	-68.3	20
1d	(<i>S</i>)	+90.3	-95.5	+109.4	20
1e	(<i>R</i>)	-112.8	+132.4	-204.3	20
1f	(<i>S</i>)	+73.9	-82.2	+141.2	20
1g	(1 <i>R</i> ,2 <i>S</i> ,5 <i>R</i> , methyl <i>R</i>)	-41.1	-120.0	+81.1	21
1h	(1 <i>R</i> ,2 <i>R</i> ,3 <i>R</i> ,5 <i>S</i> , methyl <i>R</i>)	-51.3	+38.4	-136.0	22
1i	(1 <i>R</i> ,2 <i>R</i> ,4 <i>S</i> , methyl <i>S</i>)	-72.0	+37.5	-63.5	22

opposite sign. This behaviour seems to be quite general for the ferrocenylalkyl compounds, but we cannot at present suggest an explanation for it.

Like other isocyanides, compounds **3** readily form complexes with transition metals. We have prepared the chromium pentacarbonyl complexes **4a–4c** by the reaction of $\text{Cr}(\text{CO})_5(\text{THF})$ [24] with the isocyanides **3a**, **3b**, and **3g** in THF. The products **4** are well-defined air-stable compounds. Except for the ferrocenylmethyl isocyanide complex **4b**, they can easily be purified by chromatography on silica gel. Like their parent compounds **3**, they show the expected ^1H NMR spectral data which are listed in Table 3, and IR spectral data, which are listed in Table 4 together with the spectra of two other complexes, for comparison.

The spectral data clearly reflect the electron-donating properties of the ferrocene system. In the IR spectra the characteristic stretching frequencies of the isocyano group are in the normal range for alkyl isocyanides in the ferrocenylalkyl compounds **3b–3j**, while in isocyanoferrocene **3a**, it is even lower than in aromatic isocyanides. The same is true for the pentacarbonylchromium complexes of these isocyanides. The influence on the carbonyl stretching frequencies in the complexes **4a–4b** is less pronounced. In the case of the ferrocenyl substituted vinylic isocyanide **3k**, the stretching frequency of the isocyano group lies within the range generally observed for compounds of this type ($2100\text{--}2120\text{ cm}^{-1}$) [27,28], indicating that the electron-donating effect of the ferrocene is not transmitted through the double bond.

A more detailed insight into the interaction of the donating properties of the ferrocene system and the accepting properties of the isocyano group can be expected to be provided by electrochemical experiments. Thus the isocyanides **3a**, **3b** and **3g**, as well as their chromium carbonyl complexes **4a–4c**, were studied by cyclic voltammetry in acetonitrile/ 0.2 M $[\text{NBu}_4][\text{BF}_4]$, and the results are shown in Table 5.

As expected, the isocyanides show reversible one-electron oxidations corresponding to an $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ transition. The half-wave oxidation potentials $E_{1/2}^{\text{ox}}$ fall in the usual range observed for other substituted ferrocene compounds, and clearly reflect the electron-donating or -accepting properties of the substituents [29,30]. The

Table 3

¹H NMR spectra of the compounds **3** and **4**^a, in CDCl₃ at 200 MHz. δ values (ppm), J in Hz

Compound	H(1') (s, 5H)	H(2-5), α-H	R (except α-H)
3a	4.24	4.04 ("t", 2H); 4.67 ("t", 2H)	—
3b	4.22	4.18 (m, 2H); 4.26 (m, 2H); 4.31 (m, 2H)	—
3c	4.14	4.07 (m, 4H); 4.42 (q, 1H, J 6.6)	1.44 (d, 3H, J 6.6)
3d	4.24	4.08 (m, 3H); 4.35 (m, 2H)	0.88(d)+0.96(d); (J 4.4; 6H); 1.84 (m, 1H)
3e	4.07	3.97 (m, 4H); 4.23 (m, 1H)	0.80 (s, 9H)
3f	4.24	4.08 (m, 3H); 4.33 (m, 2H)	1.10 (m, 6H); 1.30– 1.80 (m, 5H)
3g	4.24	4.02 (m, 1H); 4.14 (m, 1H); 4.18 (m, 1H); 4.37 (m, 1H); 4.84 (m, 1H)	0.81 (d, 3H, J 7.3); 0.81 (d, 3H, J 6.1); 1.00 (d, 3H, J 7.0); 0.90 (m, 2H); 1.20 (m, 1H); 1.25–1.45 (m, 4H); 1.70 (m, 2H); 2.09 (m, 1H)
3h	4.24	4.15 (m, 2H); 4.19 (m, 1H); 4.42 (m, 1H); 4.50 (m, 1H)	0.72 (d, 3H, J 6.8); 0.93 (s, 3H); 1.17 (s, 3H); 0.79 (d, 1H, J 10.0); 1.60–2.25 (m, 7H)
3i	4.27	4.12 (m, 1H); 4.18 (m, 2H); 4.24 (m, 1H); 4.30 (m, 1H)	0.80 (s, 3H); 0.85 (s, 3H); 1.13 (s, 3H); 0.70 (dd, 1H, J 12.6, 5.0); 1.20–2.00 (m, 7H)
3j	4.25	4.19 (m, 3H); 4.34 (m, 1H); 4.61 (dd, 1H, J 5.4, 7.2)	3.41 (s, 3H); 3.54 (m, 2H)
3k	4.23	4.63 (m, 2H); 4.92 (m, 2H); 7.55 (s, 1H)	3.90 (s, 3H)
4a	4.31	4.14 (m, 2H); 4.56 (m, 2H)	—
4b	4.27	4.26 (m, 4H); 4.57 (s, 2H)	—
4c	4.24	4.05 (m, 1H); 4.18 (m, 1H); 4.28 (m, 2H); 4.95 (m, 1H)	0.83 (d, 6H, J 4.8); 1.03 (d, 3H, J 6.8); 1.70 (m, 2H); 2.10 (m, 1H); 0.65–1.55 (m, 7H)

^a H(1') unsubstituted cp; H(2-5) substituted cp.

presence of an *sp*³ hybridized carbon atom between the ferrocene and the isocyano group allows transmission only of inductive effects, and the $E_{1/2}^{\text{ox}}$ values for the compounds **3b** and **3g** (0.60 and 0.62 V vs. SCE) (SCE = saturated calomel electrode) are therefore similar to that for ferrocene (0.55 V vs. SCE). The ¹H NMR spectra which show the normal pattern of substituted ferrocenes are consistent with this. Isocyanoferrocene **3a**, however, with its isocyano group directly connected with the ferrocene system, exhibits a much higher $E_{1/2}^{\text{ox}}$ (0.85 V vs. SCE), comparable

Table 4

IR spectra of pentacarbonylchromium isocyanide complexes RNC Cr(CO)₅ (cm⁻¹)

Com- pound	R	Solvent	$\nu(\text{NC})$	$\nu(\text{CO})$		3 ($\nu(\text{NC})$, free)
4a	Fc	CCl ₄	2135(s)	2055(s)	1950(vs)	2120 (CCl ₄)
4b	Fc-CH ₂	CCl ₄	2165(s)	2065(s)	1945(vs)	2145 (KBr)
		KBr	2185(s)	2065(s)	1930(vs)	
4c	Fc-CH(Men) 4-MePh [25] PhCH ₂ [26]	CCl ₄	2155(s)	2060(s)	1945(vs)	2135 (CCl ₄)
		hexane	2140	2058	1966	2130 (film)
		KBr	2190(s)	2070(s)	1955(vs)	2150 (film)
5	[Fc-CH ₂][BF ₄]	KBr	2105(s)	2060(s)	1915(vs)	-

with cyanoferrocene (0.89 V vs. SCE). This effect is probably due to the interaction of the π^* orbital of the isocyanato group with the π -system of the ferrocene. A related type of interaction, although involving the p_z orbital of a sp^2 hybridised carbene carbon atom, has been reported for ferrocenylcarbene complexes, e.g. (CO)₅Cr=C-(Fc)(OEt) which displays $E_{1/2}^{\text{ox}}$ at a value 0.31 V above that of ferrocene [30,31]. The ¹H NMR spectrum of **3a** is very similar to that of cyanoferrocene, and confirms the electrochemical observation that cyano and isocyanato group have similar electron accepting strengths.

The influence of the complexation by the (CO)₅Cr moiety is clearly seen in the IR spectra, where $\nu(\text{NC})$ is observed at values 20 cm⁻¹ higher than for the free isocyanide, but less pronounced in the ¹H NMR spectra, where only for **4b** is there a considerable downfield shift of the alkyl group.

The chromium complexes **4** exhibit two successive reversible one-electron anodic waves in the cyclic voltammograms. The number of electrons involved was estimated by comparing the current functions with that for cyanoferrocene, which is known to correspond to a single electron process, and the results were confirmed by a controlled potential electrolysis of **4b** at the first anodic wave.

The half-wave oxidation potentials of the first waves show values very close to those observed for the free isocyanides, and are therefore assigned to the ferrocene

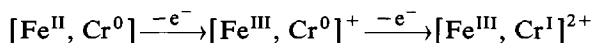
Table 5

Cyclic voltammetric data ^a for isocyanides **3a**, **3b** and **3g** and their pentacarbonyl chromium complexes **4a-4c**

compound	$I E_{1/2}^{\text{ox}}$ (V)	$I E_p^{\text{ox}}$ (V)	$I \Delta E$ (mV)	Rev. ^b	$II E_{1/2}^{\text{ox}}$ (V)	$II E_p^{\text{ox}}$ (V)	$II \Delta E$ (mV)	Rev. ^b	P_L ^c
3a ^d	0.85	0.90	110	0.8	-	-	-	-	-
3b ^e	0.60	0.64	80	0.9	-	-	-	-	-
3g ^e	0.62	0.69	140	0.9	-	-	-	-	-
Fc-CN ^{d,f}	0.89	0.93	80	1.0	-	-	-	-	-
4a ^d	0.85	0.90	100	0.9	1.31	1.37	120	0.8	-0.22
4b ^e	0.67	0.72	100	0.9	1.25	1.30	100	0.9	-0.28
4c ^e	0.65	0.69	80	1.0	1.25	1.30	100	1.0	-0.28

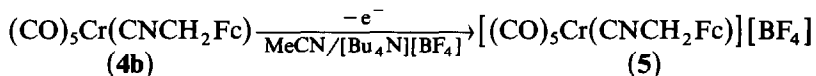
^a Values of E in volt (± 0.02) relative to SCE, measured at 100 mV/s in 0.2 M [Bu₄N][BF₄]/acetonitrile with a platinum wire electrode. ^b Reversibility ($i_p^{\text{red}}/i_p^{\text{ox}}$). ^c P_L of the oxidized ligand. ^d FcH^{0/+} couple as internal standard (E^{ox} 0.545 V vs. SCE). ^e Fc-CN^{0/+} couple as internal standard (E^{ox} 0.89 V vs. SCE). ^f Cyanoferrocene, for comparison.

system, while the second oxidations at much higher potentials (1.25–1.31 V vs. SCE) are attributed to the chromium centre (Cr^0/Cr^1):



This assignment is confirmed by comparison of the $E_{1/2}^{\text{ox}}$ of the second anodic wave with the half-wave potentials of the known [32] complex $(\text{CO})_5\text{Cr}(\text{CNMe})$ which exhibits a very similar value (1.10 V). Complexes of the type $(\text{CO})_5\text{CrL}$ (L = two-electron donor ligand, such as CO [33], $\text{P}(\text{OPh})_3$ [34], PPh_3 [34]) are oxidized generally at potentials in this range (1.53, 1.32 or 1.15 V vs. SCE, respectively).

The controlled potential electrolysis of **4b** at the first anodic wave affords a dark brown species. On the basis of its IR spectrum it can be identified as the cationic complex **5**:



Comparison of the data for **4b** and **5** shows that the $\nu(\text{NC})$ frequency is considerably lowered by the oxidation (2185 vs. 2105 cm^{-1}), while the carbonyl stretching vibration remains nearly unchanged. This also confirms that the ferrocene system is the site of the first oxidation, since the influence of the lowered net electron donor/acceptor character of the oxidized group remains limited to the iron. If the site of the first oxidation were the chromium centre, the resulting considerable increase in its electron acceptor character would lead to a shift of the $\nu(\text{CO})$ frequencies and less pronounced shifts of the $\nu(\text{NC})$ frequencies to higher wave-numbers.

For a quantitative measure of the net donor/acceptor character of a ligand, the parameter P_L has been suggested [35], where P_L is defined by the following equation:

$$P_L = E_{1/2}^{\text{ox}}[(\text{CO})_5\text{CrL}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6] \quad (\text{volt})$$

Ligands with stronger net electron donor character than the reference ligand CO have negative values of P_L . For the oxidized isocyanides as ligands, the parameters fall in a narrow range (–0.22 to –0.28 V) which indicates that they do not differ much in their donor/acceptor properties. However, they are considerably less negative than those of neutral isocyanide ligands (e.g. CNMe , P_L –0.43 V). Thus, the introduction of a positive charge in the ferrocene system has a positive effect on the P_L parameter of about 0.2 V, since the neutral ferrocene group has similar electron donor abilities as the methyl group [36]. The cationic ferrocenium isocyanides studied so far are better electron acceptors than PPh_3 (P_L = –0.35 V), but weaker than $\text{P}(\text{OPh})_3$, N_2 or CO with P_L –0.18, –0.07 and 0.00 V, respectively).

Preliminary studies have been made of the organic chemistry of the ferrocene isocyanides. They seem to undergo normal α -addition reactions like four component condensations [8], but attempts to bring about carbanion reactions have so far been unsuccessful. The carbanion stabilizing ability of the isocyanide group is probably not sufficient to compete with the donor properties of the ferrocene system. Details of this chemistry, particularly of asymmetric inductions by the chiral isocyanides, will be presented elsewhere.

Experimental

^1H NMR spectra were recorded on a Bruker WP 200 spectrometer and IR spectra on a Perkin-Elmer 157 spectrophotometer. Electrochemical measurements were performed with a EG&G PAR 173 potentiostat/galvanostat and a EG&G PAR 175 universal programmer. All new compounds, except **4b** and **5**, give correct microanalytical data, which are listed in Table 6. Owing to its instability towards chromatography, **4b** could not be obtained pure.

General method for the preparation of the formamides 2 from the amines 1

The amine **1** (10 mmol) is refluxed with ethyl formate (30 ml) until the starting amine has completely disappeared (TLC monitoring; about 2 days). The mixture is

Table 6
Microanalytical data of new compounds.

Compound	Formula	(Found (calcd.)(%))		
		C	H	N
2a	$\text{C}_{11}\text{H}_{11}\text{FeNO}$	57.57	4.94	6.03
		(57.68)	(4.84)	(6.11)
2c	$\text{C}_{13}\text{H}_{15}\text{FeNO}$	60.57	5.99	5.31
		(60.73)	(5.88)	(5.45)
2d	$\text{C}_{15}\text{H}_{19}\text{FeNO}$	63.30	6.52	4.86
		(63.18)	(6.72)	(4.91)
2e	$\text{C}_{16}\text{H}_{21}\text{FeNO}$	63.99	6.95	4.74
		(64.23)	(7.07)	(4.68)
2g	$\text{C}_{22}\text{H}_{31}\text{FeNO}$	69.34	8.30	3.64
		(69.29)	(8.19)	(3.67)
2i	$\text{C}_{22}\text{H}_{29}\text{FeNO}$	69.35	7.84	3.64
		(69.66)	(7.70)	(3.69)
3a	$\text{C}_{11}\text{H}_9\text{FeN}$	62.70	4.34	6.45
		(62.60)	(4.30)	(6.64)
3b	$\text{C}_{12}\text{H}_{11}\text{FeN}$	63.88	5.08	6.01
		(64.04)	(4.93)	(6.22)
3c	$\text{C}_{13}\text{H}_{13}\text{FeN}$	65.15	5.40	5.77
		(65.30)	(5.48)	(5.86)
3d	$\text{C}_{15}\text{H}_{17}\text{FeN}$	67.53	6.31	5.03
		(67.44)	(6.41)	(5.24)
3e	$\text{C}_{16}\text{H}_{19}\text{FeN}$	68.21	6.79	5.08
		(68.35)	(6.81)	(4.98)
3g	$\text{C}_{22}\text{H}_{29}\text{FeN}$	72.61	8.16	3.78
		(72.73)	(8.04)	(3.85)
3i	$\text{C}_{22}\text{H}_{27}\text{FeN}$	73.29	7.53	3.65
		(73.13)	(7.53)	(3.88)
4a	$\text{C}_{16}\text{H}_9\text{CrFeNO}_5$	48.58	2.11	3.39
		(48.77)	(2.30)	(3.55)
4b	$\text{C}_{17}\text{H}_{11}\text{CrFeNO}_5$	49.40	2.31	2.89
		(48.95)	(2.66)	(3.36)
4c	$\text{C}_{27}\text{H}_{29}\text{CrFeNO}_5$	62.50	4.96	2.39
		(62.72)	(5.26)	(2.52)
5	$\text{C}_{17}\text{H}_{11}\text{BCrF}_4\text{FeNO}_5$	42.05	2.51	2.99
		(41.68)	(2.16)	(2.73)

diluted with dichloromethane (100 ml) and extracted with water and the extract is dried (Na_2SO_4) and evaporated. The residue is treated with hexane (50 ml) and the insoluble formamides filtered off and dried in vacuum. The yields and properties of the products are shown in Tables 1, 2, and 6.

Preparation of the isocyanides 3 from the formamides 2 [20]

The formamide **2** (10 mmol) and dry diisopropylamine (27 mmol) are dissolved in dry dichloromethane (15 ml), and phosphoryl chloride (11 mmol) is added dropwise with stirring at 0°C with exclusion of moisture. After 1 h stirring at 0°C for a solution of sodium carbonate (2.0 g) in water (10 ml) is added dropwise at room temperature. After another hour stirring more water and dichloromethane are added and the organic phase is separated and washed with water, dried with Na_2SO_4 , then evaporated, and the residue is recrystallized from hexane or purified by extraction with hexane (compounds **3c** and **3d**). For yields and properties, see Tables 1–3 and 5–6.

Preparation of the chromium carbonyl complexes 4

A solution of $\text{Cr}(\text{CO})_6$ (1.0 mol, 0.22 g) in dry THF (200 ml) is saturated with nitrogen and irradiated for 2 h with a Hanau TQ mercury high pressure lamp (quartz filter). The isocyanide (1.0 mmol) is added and the mixture is stirred for 1 h. After filtration, followed by evaporation of the solvent, the residue is either purified by preparative TLC (silica gel, hexane) or, in the case of compound **4b**, by precipitation of the impurities with diethyl ether then filtration and evaporation of the solution and repetition of the procedure. The IR spectral data are listed in Table 4, ^1H NMR spectra in Table 3, electrochemical data in Table 5, and microanalytical data in Table 6.

4a: Yield 85%, m.p. $103\text{--}104^\circ\text{C}$. **4b**: Yield 55%, m.p. $84\text{--}88^\circ\text{C}$. **4c**: Yield 76%, oil. $[\alpha]_{\text{D}}^{20} = +273.6$ (c 0.2, EtOH).

Oxidation of complex 4b

A solution of **4b** (21 mg, 0.05 mmol) in 0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ /acetonitrile (15 ml) was electrolysed at $E_{\text{p}}^{\text{ox}} = 0.64$ V vs. SCE with a platinum electrode. The electrolysis was complete after 4 h. After concentrating the solution to about 5 ml and addition of 0.5 ml of water, product **5** separated out and was filtered off and dried in vacuum.

5: Yield 20 mg (80%), m.p. $286\text{--}288^\circ\text{C}$.

Acknowledgement

The authors thank Prof. Dr. I. Ugi, TU München, for supporting this work. A grant from Deutscher Akademischer Austauschdienst (to T. El-Shihi) and financial support from Deutsche Forschungsgemeinschaft and Instituto Nacional de Investigación Científica are gratefully acknowledged.

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