Unfortunately, unlike the νWH band, the νReH band is not detected in the IR spectra of hydride **1**.[1a] The evidence for the formation of a hydrogen bond of the ReH...HOR type was obtained in studying the interaction of **1** with $(CF_3)_3COH$ in liquid freon (CDF_2/CDF_2Cl) by the ^1H NMR method; the high effectiveness of using liquid freon at very low temperatures (down to 96 K) was shown previously in a study of hydrogen bonds with organic bases.[6] A high-field shift (by 0.60—0.82 ppm) of the signal of the hydride hydrogen ($\delta_{init} = -7.54$) that depended on the temperature and the amount of excess proton donor was observed in the spectra of **1** in the presence of $(CF_3)_3COH$ in the temperature range from 140 to 110 K. At 96 K, we succeeded for the first time in detecting splitting of the hydride signal into two signals (at δ −7.54 and −8.87) corresponding to free ReH and the ReH...HO complex, respectively. This proves that the formation of the hydrogen bond involves the hydride hydrogen. Note that in this case the signal of the OH group is split into three signals (at δ 5.6, 9.8, and 8.2) corresponding to the OH groups of the monomer, the OH...HRe complex, and the OH...ON complex, respectively.

Thus, rhenium hydride **1** forms hydrogen bonds of two types with R^FOH, namely, bonds with the oxygen atom of the NO group (NO...HO) and bonds with the hydride hydrogen (ReH...HO).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34114), and by the Russian Foundation for Basic Research and INTAS (Grant No. 95-136).

References

1. (a) E. S. Shubina, N. V. Belkova, A. N. Krylov, E. V. Vorontsov, L. M. Epstein, D. G. Gusev, M. Niedermann, and H. Berke, *J. Am. Chem. Soc.*, 1996, **118**, 1105; (b) E. Peris, J. Wessel, B. P. Patel, and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1995, 2175.
2. M. S. Chinn, D. M. Heinekey, N. G. Payne, and C. D. Sofield, *Organometallics*, 1989, **8**, 1824.
3. A. T. Patton, C. E. Strouse, C. B. Knobler, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1984, **105**, 5804
4. N. E. Kolobova, I. A. Lobanova, V. I. Zdanovich, and P. V. Petrovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 935 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 707 (Engl. Transl.)].
5. I. A. Lobanova, V. I. Zdanovich, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 691 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 642 (Engl. Transl.)].
6. (a) N. S. Golubev and G. S. Denisov, *J. Mol. Struct.*, 1992, **270**, 263; (b) N. S. Golubev, S. N. Smirnov, V. A. Gindin, G. S. Denisov, H. Benedict, and H.-H. Limbach, *J. Am. Chem. Soc.*, 1994, **116**, 12055; (c) S. N. Smirnov, N. S. Golubev, G. S. Denisov, H. Benedict, P. Shah-Mohammedi, and H.-H. Limbach, *J. Am. Chem. Soc.*, 1996, **118**, 4094.
7. B. V. Lokshin, S. G. Kazaryan, and A. G. Ginzburg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 562 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37** (Engl. Transl.)].
8. B. V. Lokshin, S. G. Kazaryan, and A. G. Ginzburg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 948 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36** (Engl. Transl.)].

Received January 20, 1997

One-step synthesis of α-hydroxy-α-azinylcyanoacetic esters from α-nitro derivatives of α-azinylcyanoacetic esters

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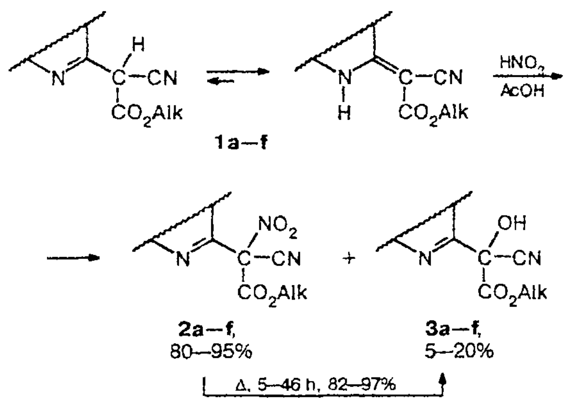
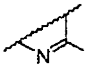
When boiled in aromatic hydrocarbons, solutions of α-nitro-α-azinylcyanoacetic esters of the pyrimidine, pyrazine, and *s*-triazine series gave the corresponding α-hydroxy derivatives of α-azinylcyanoacetic esters in high yields.

Key words: nitrocyanoacetic esters, hydroxycyanoacetic esters, pyrazine, pyrimidine, *s*-triazine, derivatives.

Previously, we have demonstrated that nitration of dihydroazinylidenecyanoacetic esters of the pyrimidine series, **1a—d**,[1] and of the pyrazine series, **1e**,[2] afforded α-hydroxy derivatives of α-azinylcyanoacetic esters **3a—e** in low yields along with α-nitro derivatives **2a—e**.

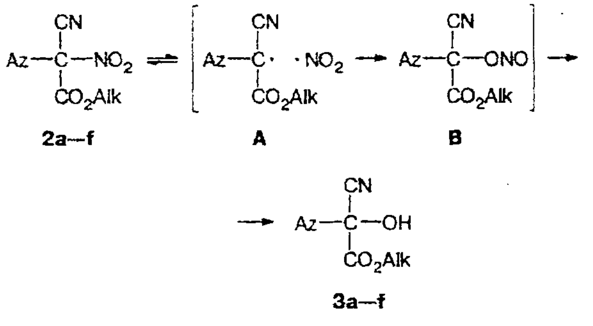
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1407—1409, July, 1997.



1—3:  = 4-phenylpyrimidinyl-2- (**a**),
5-phenylpyrimidinyl-2- (**b**),
4,6-diphenylpyrimidinyl-2- (**c**),
2-phenylpyrimidinyl-4- (**d**), 3-chloropyrazinyl-2- (**e**),
4,6-diphenyl-*s*-triazinyl-2- (**f**)

esters **3a—e** in low yields along with α-nitro derivatives **2a—e**.

In this work, it was established that α-nitroacetonitriles **2a—f** were converted to the corresponding α-hydroxy derivatives **3a—f** in yields of 82—97% when boiled in aromatic hydrocarbons. In the case of compound **2d**, brown nitrogen oxides were eliminated. In the absence of atmospheric oxygen, the time of complete conversion of nitro-substituted compounds **2a—f** in benzene substantially decreased (Table 1), which is indicative of a radical mechanism of the reaction. The scheme of conversions **2a—f**→**3a—f** is, apparently, analogous to that suggested for thermal rearrangement of α-nitro-α-arylacetonitriles[3,4] and involves formation of the radical pair **A**, recombination of radicals to nitrite **B**, homolysis of the O—NO bond, and conversion to the corresponding hydroxy derivative **3a—f**.



Unlike the phenyl analog,[4] in this case products of dimerization of substituted azinylmethyl radicals were not detected. The stability of cyanohydrins **3a—f** is attributable to the stabilizing effect of electron-withdrawing azinyl groups.[5]

Table 1. Time of complete conversion **2a—f** → **3a—f** in benzene

Compound	Alk	τ/h*		σ_I	Yields of **3a—f** (%)
		A	B		
2a	Et	32	8	0.10	94
2b	Et	18.5	5	0.11	82
2c	Et	46	12	0.10	84
2d	Me	5	1	0.19	89
2e	Et	18	4.5	—	97
2f	Et	9.5	3	0.16	97

* τ is the reaction time, A, without argon; and B, under an argon atmosphere. ** Constants of azinyl fragments were calculated for phenyl-substituted azinyl groups.[7]

The formation of minor α-hydroxy-α-azinylcyanoacetic esters **3a—d** during nitration of dihydroazinylidenecyanoacetic esters **1a—d** [1] by the HNO_3—$(MeCO)_2O$ system can be described analogously.

Using pyrimidine derivative **2d** as an example, we demonstrated that the reaction accelerated with increased temperature. Thus, the time of complete conversion of α-nitro derivative **2d** decreased from 5 to 2 h in going from benzene to toluene. Analogous acceleration of conversion **2d**→**3d** was observed in passing from an aromatic hydrocarbon (benzene) to acetonitrile, which is consistent with the regularities known for radical processes.[6]

The time for complete conversion of esters **2a—f** depends also on the type of heterocyclic substituent present in the molecule. Thus, going from derivative **2c**, which contains a diphenyl-substituted pyrimidine fragment, to compound **2a**, which has a phenylpyrimidine residue, the time of conversion decreased by almost a factor of 1.5, while going to α-nitro derivative **2f**, which contains a highly electron-withdrawing triazine fragment, caused the conversion time to decrease fivefold. Apparently, this is associated with additional stabilization of the radical pair **A** due to the inductive effect of the azinyl residues (see Table 1).

The compositions and structures of α-hydroxy derivatives **3e,f** were confirmed by the data of elemental analysis and by spectral methods. Thus, the IR spectra of compounds **3e,f**, like those of α-hydroxy derivatives **3a—d** reported previously,[1] have a carbonyl group band in the 1755—1760 cm^{-1} region and a OH group band at 3440—3490 cm^{-1}. The ^1H NMR spectra have a signal of the proton of the OH group along with signals of the protons of the aromatic and ester groups.

Experimental

The IR spectra were recorded on a UR-20 spectrophotometer using KBr pellets (the concentration was 0.25%). The

^1H NMR spectra were recorded on a Bruker WP-200 SY instrument (200.13 MHz). The chemical shifts were measured relative to the signal of the solvent.

The course of the reaction and the purities of the resulting compounds were monitored by TLC on Silufol UV-254 plates using a 10 : 1 chloroform—ethanol mixture as the solvent (a UV detector).

α-Nitro-α-(3-chloropyrazinyl-2)cyanoacetic ester (2e) was prepared by nitration of 3-chloropyrazinyl-2-cyanoacetic ester with nitric acid in acetic acid according to the procedure reported previously;[1] the yield was 85%, m.p. 46—48.5 °C (from ethanol). Found (%): C, 39.36; H, 2.57; N, 20.63; Cl, 13.22. $C_9H_7ClN_4O_4$. Calculated (%): C, 39.94; H, 2.61; N, 20.70; Cl, 13.10. IR, ν/cm^{-1}: 1775 (C=O). ^1H NMR ($CDCl_3$), δ: 1.38 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); 4.54 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 8.56 (d, 1 H, H(5), J=2.5 Hz); 8.61 (d, 1 H, H(6), J = 2.5 Hz).

α-Nitro-α-(4,6-diphenyl-*s*-triazinyl-2)cyanoacetic ester (2f) was prepared by nitration of 4,6-diphenyl-*s*-triazinyl-2-cyanoacetic ester with nitric acid in acetic acid according to the procedure reported previously;[1] the yield was 85%, m.p. 128—130 °C (from ethanol). Found (%): C, 61.60; H, 3.80; N, 17.90. $C_{20}H_{15}N_5O_4$. Calculated (%): C, 61.69; H, 3.88; N, 17.99. IR, ν/cm^{-1}: 1780 (C=O). ^1H NMR ($(CD_3)_2CO$), δ: 1.43 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); 4.68 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 7.59—7.93, 8.56—8.82 (m, 10 H, Ph).

α-Hydroxy-α-azinylcyanoacetic esters 3a—f (general procedure). Nitro derivatives **2a—f** (1 mmol) were dissolved with heating in anhydrous benzene (3 mL), and the reaction mixture was refluxed until the initial compound had completely disappeared (monitored by TLC; the times for complete conversion and the yields of the products are given in Table 1). Benzene was evaporated, and the residue was chromatographed on a column packed with silica gel (100—160 μm) using a 10 : 1 chloroform—ethanol mixture as the solvent. α-Hydroxy derivatives **3a—d** were obtained. Their melting points and IR spectra were identical to those reported previously.[1]

α-Hydroxy-α-(3-chloropyrazinyl-2)cyanoacetic ester (3e), oil. Found (%): C, 44.59; H, 3.28; N, 17.45; Cl, 14.58. $C_9H_8ClN_3O_3$. Calculated (%): C, 44.73; H, 3.34; N, 17.39; Cl, 14.67. IR, ν/cm^{-1}: 1760 (C=O), 3440 (OH). ^1H NMR ($CDCl_3$), δ: 1.31 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); 4.37 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 5.66 (br.s, 1 H, OH); 8.54 (d, 1 H, H(5), J = 2.5 Hz); 8.59 (d, 1 H, H(6), J = 2.5 Hz).

α-Hydroxy-α-(4,6-diphenyl-*s*-triazinyl-2)cyanoacetic ester (3f), m.p. 148—151 °C (from a 3 : 1 pentane—benzene mixture). Found (%): C, 66.35; H, 4.37; N, 15.37. $C_{20}H_{16}N_4O_3$. Calculated (%): C, 66.67; H, 4.44; N, 15.56. IR, ν/cm^{-1}: 1755 (C=O), 3490 (OH). ^1H NMR ($(CD_3)_2CO$), δ: 1.26 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); 4.40 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 5.89 (br.s, 1 H, OH); 7.56—7.80, 8.64—8.80 (m, 10 H, Ph).

This work was supported by the International Science Foundation and the Russian Federation Government (Grant NQN 300).

References

1. I. V. Oleinik and O. A. Zagulyaeva, *Sib. Khim. Zh.* [*Siberian Chem. J.*], 1992, No. 4, 117 (in Russian).
2. I. V. Oleinik and O. A. Zagulyaeva, *Mendeleev Commun.*, 1994, 50.
3. W. Hochstein and U. Schöllkopf, *Lieb. Ann. Chem.*, 1978, 1823.
4. R. Ketari and A. Foucaud, *J. Org. Chem.*, 1981, **46**, 4498.
5. H. G. O. Becker, *Einführung in die Elektronentheorie organisch-chemischer Reaktionen*, Deutscher Verlag der Wissenschaften, Berlin, 1974.
6. A. L. Buchachenko and A. M. Vasserman, *Stabil'nye radikaly* [*Stable Radicals*], Khimiya, Moscow, 1973, 396 pp. (in Russian).
7. V. P. Mamaev, O. P. Shkurko, and S. G. Baram, *Adv. Heterocycl. Chem.*, 1978, **42**, 19, 75.

Received January 22, 1997