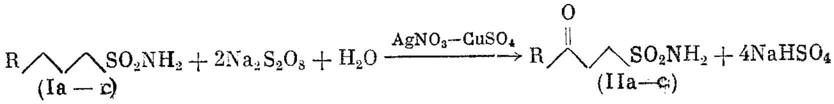

R=CH$_3$ (a), C$_2$H$_5$ (b), C$_3$H$_7$ (c).

Compound (Ia) undergoes 46% conversion to give (IIa) formed in 90% yield relative to converted (Ia). Compound (Ib) undergoes 30% conversion to give (IIb) formed in 90% yield relative to converted (Ib). Compound (Ic) undergoes 20% conversion to (IIc) formed in 100% yield relative to converted (Ic). The reaction mechanism apparently entails the generation of sulfonylamidyl radicals $R(CH_2)_3SO_2\dot{N}H$ which undergo regiospecific rearrangement with 1,5-hydrogen migration to transfer the reaction site to the nonactivated C^3 atom. Compound (II) is formed upon the oxidation of the rearranged radicals $R\dot{C}H(CH_2)_2SO_2NH_2$, probably through intermediate 3-hydroxysulfonamides $RCH(OH)(CH_2)_2SO_2NH_2$. We previously studied the long-range oxygenation of ketones in the $Na_2S_2O_8-FeSO_4$ system to form 1,4- and 1,5-diketones [3].

A sample of 0.5 g (0.002 mole) $CuSO_4 \cdot 5H_2O$ and 0.26 g (0.0015 mole) $AgNO_3$ were added to a suspension of 1.37 g (0.01 mole) (Ia) in 20 ml water and heated to 85-90°C. Then, a solution of 2.38 g (0.01 mole) $Na_2S_2O_8$ in 20 ml water was added dropwise. The reaction mixture was stirred for 5 h at 90°C, cooled, and extracted with three 30-ml portions of ether. The extract was dried over Na_2SO_4 and evaporated. The mixture of (IIa) and (Ia) obtained was treated with 2,4-dinitrophenylhydrazine, and the 2,4-dinitrophenylhydrazone of (IIa) was isolated with mp 177.5-179°C (from ethanol). Found: C 36.69; H 4.08; N 21.13; S 9.75%. Calculated for $C_{10}H_{13}N_5O_6S$: C 36.25; H 3.96; N 21.14; S 9.67%. Mass spectrum: m/z 331 (M^+). Reductive hydrolysis [4] regenerated (IIa) from its 2,4-dinitrophenylhydrazone as an oil. PMR spectrum in $CDCl_3$ at 250 MHz (δ, ppm, TMS): 2.29 s (3H), 3.22 s (4H). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm, TMS): 21.717 q (CH_3), 37.920 t and 44.382 t (CH_2CH_2), 183.24 s (C=O). Mass spectrum: m/z 151 (M^+).

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$[(CH_3)_3NH][Rh_2I_7]$ AS A CATALYST FOR THE CONVERSION OF CARBON MONOXIDE AND CARBONYLATION OF METHANOL

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Rhodium compounds are catalysts for several reactions involving carbon monoxide [1, 2]. In the present work, we report the synthesis of a catalytically active rhodium complex prepared by the reaction of a solution of $[(CH_3)_3NH]_3[RhCl_6] \cdot 3H_2O$ (I) in DMF acidified with hydrochloric acid, with analytical-grade (45.1%) hydriodic acid upon heating. We used 2 g (I), 100 ml DMF, 5 ml hydrochloric acid, and 25 ml hydriodic acid. These components were heated at 80-100°C for 30 min. The complex product was isolated as a black powder, washed on a filter with ethanol and ether, and dried at 20°C (0.1 mm) for 3 h. The yield was 90%. The IR spectral and elemental analysis data indicate that this complex is $[(CH_3)_3NH][Rh_2I_7]$ (II). Found: Rh 17.7; C 3.4; H 1.3; N 1.5; I 76.0%. Calculated for $Rh_2C_3H_{10}NI_7$: Rh 17.84; C 3.12; H 0.86; N 1.21; I 76.97% IR spectrum (ν, cm^{-1}): 800 (CN), 1010 (Rh), 1450 (CH_3), 1595 (NH), 3085 (NH). Complex (II) decomposes without melting above 300°C, is nonhygroscopic, and is soluble in DMF.

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The catalytic properties of (II) are comparable with those of other rhodium compounds. Thus, the activity of (II) in the conversion of CO with water is 2.8 mole H_2/g-atom Rh·h (46 mg (II), 13 ml AcOH, 6 ml HCl, 6 ml H_2O, 8.4 g NaI, 600 mm, 90°C). The conversion was 51% in the carbonylation of methanol in acetic acid using 17.8 mg (II), 20 ml HI, 9.3 ml CH_3CH_2COOH, and 0.4 ml methanol at 185°C, 30 atm for 2 h.

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A STABLE SEMIACETAL NOT CONTAINING ELECTRONEGATIVE SUBSTITUENTS AT THE CARBON ATOM

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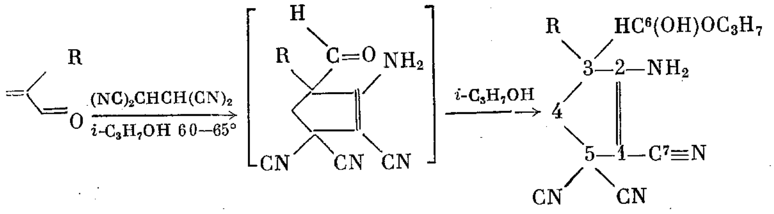
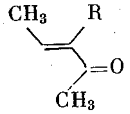
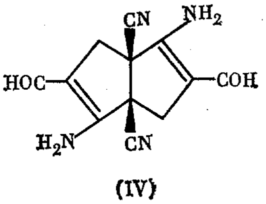
Compounds with acyclic semiacetal or gem-diol fragments are unstable and may be isolated from solution only in rare cases [1]. We have prepared (II) with a stable semiacetal fragment according to the following scheme:



(II, a, b)



(III)



(IV)

R=CH_3 (a), C_2H_5 (b)

The structure of (IIb) was proven by x-ray diffraction structural analysis. The unit-cell parameters for these crystals are: a = 7.932(2), b = 12.860(2), c = 16.282(3) Å, γ = 113.92(2)°, space group $P2_1/b$, Z = 4, d_{calc} = 1.20 g/cm³. The structure was solved on a RÉD-4 diffractometer using Cu K_α radiation for 1564 reflections by the direct method and full-matrix refinement, R = 0.050. Compounds (IIa) and (IIc) are stable in DMSO-d_6. The ^{13}C NMR spectra of (IIa) and (IIb) were taken on a WH-90 spectrometer at 22.63 MHz with HMDS as the standard. (IIa): 66.2 (C^1), 171.8 (C^2), 54.2 (C^3), 41.5 (C^4), 37.7 (C^5), 95.1 (C^6), 116.0 (C^7), 117.2 and 116.2 (gem-dicyano groups). (IIb): 67.8 (C^1), 169.6 (C^2), 59.3 (C^3), 37.9 (C^4), 38.1 (C^5), 95.2 (C^6), 115.9 (C^7), 117.1 and 116.3 (gem-dicyano group). The stability of the semiacetal fragment may be a consequence of the diminished activity of the oxygen atom due to coordination of this atom by C^2 [O...C^2, 2.772(2) Å] and carbon atom of the cis-nitrile group [O...C, 3.010(2) Å]. We should note that the Michael condensation of 1,1,2,2-tetracyanoethane with trans-α, β-unsaturated ketones (III) and acrolein in aqueous ethanol leads to compounds such as (I) [2] and (IV) (proven by x-ray diffraction structural analysis).

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