REACTION OF FLUORINATED ALDEHYDES WITH PHENYLACETYLENE

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Nonfluorinated aldehydes do not react with acetylenes in the absence of catalysts but upon UV irradiation or in the presence of stoichiometric amounts of BF₃ etherate, these compounds undergo [2 + 2] cycloaddition to form α,β -unsaturated ketones (UK). It has been proposed that this reaction proceeds through the formation of oxetenes

$$X = 0, S.$$

$$RC \equiv CXR^{1} + C = 0 \rightarrow \begin{bmatrix} R \\ C \equiv C \\ C \end{bmatrix} \xrightarrow{C} 0 \begin{bmatrix} R \\ C = CC \\ C \end{bmatrix} \xrightarrow{C} C = CC \\ 0 \end{bmatrix}$$

$$(1)$$

In the presence of basic catalysts such as KOH, NaNH₂ and metal acetylides, nonfluorinated aldehydes add to acetylenes to form acetylenic alcohols (AA) [2].

We have found that in contrast to nonfluorinated aldehydes, their fluorinated analogs (I) react with phenylacetylene without catalyst to form a mixture of UK (II) and AA (III).

$$R_{\mathbf{F}}C \xrightarrow{t^{\circ}} R_{\mathbf{F}}CH = CH \xrightarrow{t^{\circ}} R_{\mathbf{F}}CH = CH - C - Ph + Ph - C \equiv C - CH - R_{\mathbf{F}}$$
(2)

$$H \xrightarrow{(Ia-B)} (IIa-c) \xrightarrow{(IIIa-c)} OH$$

$$R_{\mathbf{F}} = -\frac{F_{\alpha}}{C - (CF_{2})_{n}X}; X = H, n = 3(a); X = H, n = 5(b); X = F, n = 5(c).$$

UK (IIa)-(IIc) are not the products of the isomerization of AA since the latter are unaltered under the conditions of reaction (2). The isomerization of AA (IIIa) and (IIIb) to UK (IIa) and (IIb) was accomplished only upon heating at reflux for 30 h in 30% acetic acid (Meyer-Schuster isomerization [2]). The formation of UK and AA apparently proceeds by independent pathways and is a consequence, on one hand, of the enhanced electrophilicity of the aldehydic carbon atom of fluorinated aldehydes and, on the other, the labile methine hydrogen atom of phenylacetylene. The structure of UK (IIa)-(IIc)* is in accord with the oxetene mechanism for the reaction of acetylenes with aldehydes [1]. The fraction of UK in the mixture decreases with increasing length of the fluoroalkyl substituent of the aldehyde. The formation of AA is not observed upon the reaction of 7-monohydroperfluoroheptanal with phenylacetylene in the presence of an equimolar amount of BF₃ etherate according to Bos and Arens [3]. Unreacted fluorinated aldehyde as the hydrate was isolated along with UK (IIb).

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-567 spectrometer in $CDCl_3$ relative to TMS. The IR spectra were taken neat (20 μ m pathlength) for liquids and in vaseline mull for solids on a Specord-75 IR spectrometer. Samples of the polyfluorinated aldehydes were obtained according to Pierce and Kane [6].

*UK (IIa)-(IIc) were shown identical by thin-layer chromatography and IR and PMR spectroscopy to trans-UK obtained in our previous work by the aldol condensation of fluorinated aldehydes with the corresponding methyl ketones [4] and the condensation of fluorinated aldehydes (Ia)-(Ic) with unsymmetrical polyfluorinated β -diketones [5].

Institute of Chemistry, Urals Science Center, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 212-214, January, 1987. Original article submitted April 1, 1986. Reaction of 5-monohydroperfluoroheptenal (Ia) with phenylacetylene. A mixture of 6.8 g (30 mmoles) (Ia) and 3 g (30 mmoles) phenylacetylene was heated at reflux. The extent of the reaction was monitored by thin-layer chromatography on Silufol UV-254 plates treated with KMnO4 solution. The reaction mass was separated by chromatography on a column packed silica gel L 40/100. Elution with hexane gave 6 g (62%) 1-phenyl-4,4,5,5,6,6,7,7-octafluoro-2-hepten-1-one (IIa), bp 104°C (5 mm). Found: C 47.21; H 2.30; F 45.63%. Calculated for $C_{13}H_{0}F_{0}O: C 47.01; H, 2.43; F 45.75\%$. IR spectrum (ν , cm⁻¹); 1630 (C=C), 1680 (C=O). PMR spectrum (δ , ppm): 6.09 t. t(J_{HCF2} = 54, J_{HCF2}CF2 = 5.6 Hz), 6.6-7.1 m (CH=CH), 7.2-8.1 m (Ph).

Chloroform elution gave 1.98 g (20%) 1-pheny1-4,4,5,5,6,6,7,7-octafluoro-1-heptyn-3-ol (IIIa) as an oil. Found: C 47.42; H 2.57%. Calculated for $C_{13}H_8F_80$: C 47.01; H 2.43%. IR spectrum (v, cm⁻¹): 2250 (C=C), 3200-3600 (OH). PMR spectrum (δ . ppm): 3.36 s (OH, disappears upon the addition of CF_3CO_2D), CH AB system: 5.08 d ($J_{HF\alpha} = 12$ Hz), 5.2 d ($J_{HF\beta} = 12$ Hz), 6.08 t. t ($J_{HCF_2} = 54$, $J_{HCF_2}CF_2 = 6$ Hz), 7.2-7.6 m (Ph).

2) A mixture of 13.3 (4.4 mmoles) (Ib), 4.5 g (4.4 mmoles) phenylacetylene and 6.2 g (4.4 mmoles) BF₃ according to Bos and Arens [3] gave 3.8 g (20%) (IIb) and 6 g (42%) hydrate of (Ib) (identical in its melting point and IR spectrum to an authentic sample).

Reaction of perfluoroheptenal (Ic) with phenylacetylene. By analogy, 6.9 g (20 mmoles) (Ic) and 2 g (20 mmoles) phenylacetylene gave: a) 1.7 g (19%) 1-phenyl-3-perfluorohexyl-2propen-1-one (IIc), bp 110°C (5 mm). Found: C 40.40; H 1.62%. Calculated for $C_{13}H_7F_{13}O$: C 40.03; H 1.56%. IR spectrum (ν , cm⁻¹): 1630 (C=C), 1685 (C=O). b) 5.5 g (62%) 1-phenyl-3-perfluorohexyl-1-propyn-3-ol (IIIc), mp 53-54°C. Found: C 40.25; H 1.50%. Calculated for $C_{13}H_7F_{13}O$: C 40.02; H 1.56%. IR spectrum (δ , cm⁻¹): 2230 (C=C), 3100-3600 (OH).

Isomerization of 1-pheny1-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1-nonyn-3-o1 (IIIb). a) A sample of 0.5 g (1.5 mmoles) (IIIb) was heated in a sealed ampul for 15 h at 145°C. Monitoring by thin-layer chromatography indicated the absence of (IIb) in the reaction. Chromatography on a silica gel column with elution by CHCl₃ gave 0.45 g (90%) starting (IIIb).

b) A mixture of 1 g (3 mmoles) (IIIb) and 0.3 g (3 mmoles) phenylacetylene was heated at reflux for 30 h. Monitoring by thin-layer chromatography indicated the absence of (IIb) in the reaction mass. Column chromatography gave 0.96 g (96%) (IIIb).

c) A sample of 1 ml distilled water and 0.5 ml acetic acid were added to 0.5 g (1.5 mmole) (IIIb). The reaction mass was heated at reflux with monitoring of the extent of the reaction by thin-layer chromatography. Chromatography on a silica gel column with hexane elution gave 0.4 g (80%) (IIIb) which was identical in its thin-layer chromatography and IR spectrum to an authentic sample.

CONCLUSIONS

Fluorinated aldehydes add to phenylacetylene with the formation of mixtures of α,β -unsaturated fluoroketones and acetylenic fluoroalcohols.

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SYNTHESIS AND STRUCTURE OF CHLORONITROACETAMIDE COMPLEXES WITH Cu²⁺ AND N1²⁺ IONS

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Salts of aliphatic acinitro compounds, as a rule, are unstable [1, 2]. Stable compounds in this series would hold interest for the study of the structure and applications of such compounds. The molecular and crystal structure of the dimethylammonium salt of ethyl chloronitroacetate and the ammonium salt of chloronitroacetamide (CNA) were determined by x-ray diffraction structural analysis [4-6] among the prepared derivatives of chloronitroacetic acid [3, 4]. However, these compounds do not have sufficient stability and decompose within 1-2 months.

In the present work, we describe the preparation and properties of compounds of CNA with Cu^{2+} and Ni^{2+} ions

$$\begin{split} \mathbf{M} \cdot (\mathbf{O}_2 \mathbf{N} = \text{CCICONH}_2)_2 \cdot (\mathbf{NH}_3)_n \cdot \mathbf{X} \\ \mathbf{M} = \mathbf{Cu}; \ n = 4(\mathbf{I}); \ n = 2(\mathbf{II}); \ n = 0, \ \mathbf{X} = \mathbf{H}_2 \mathbf{O}(\mathbf{III}); \ \mathbf{M} = \mathbf{Ni}, \ n = 0, \\ \mathbf{X} = \text{EtOH} \ (\mathbf{IV}). \end{split}$$

The reaction of the ammonium salt of CNA with $(AcO)_2Cu$ in the presence of a 20-fold excess of aqueous NH₃ led to bis(chloronitroacetamidato)tetramminecopper(II) (I) in yields up to 50%. Under the same conditions, the reaction with cupric sulfate gives 5% (I). The use of a two-fold excess of aqueous ammonium leads to diammine derivative (II). Attempts to obtain ammine complexes using nickelous acetate and nitrate were unsuccessful even by increasing the reaction time by a factor of 6-8. Bischloronitroacetamidate compounds of (III) and (IV) are readily obtained in ethanolic medium upon heating.

Complexes (I)-(IV) do not alter their color, decomposition temperature, and IR spectrum for at least six months in a transparent vessel in the light. Complex (III) upon the action of water or ammonium vapor turns green, which, in all likelihood, is related to its conversion to more highly coordinated compounds.

X-ray diffraction structural analysis shows that the cupric ion in the centrosymmetric molecule of (I) is in a square composed of four NH_3 molecules (the mean Cu-N bond length is 2.008 Å) and its coordination is augmented to octahedral by the oxygen atoms of the two trans monodentate ligands L = $(O_2N = CCICONH_2)$ (Fig. 1). The monodentate function of ligand L is achieved through the oxygen atom of the nitro group which simultaneously participates in an intraligand O...H-N hydrogen bond. The coordination of the Cu²⁺ by ligands is markedly ionic in nature. The distribution of the bond lengths and the planarity of ligand L indicates the existence of π -conjugation [6].

EXPERIMENTAL

CNA and its ammonium salt were obtained according to our previous procedure [4]. A sample of chloroform was dried over CaCl₂ and distilled. The other reagents and solvents were not subjected to additional purification. Thermal stability was determined on glass slides using a Boetius apparatus. The IR spectra were taken as vaseline mulls on a Specord IR-75 spectrometer.

Bis(chloronitroacetamidato)tetramminecopper(II) (I). A sample of 12 ml 25% aqueous NH₃ was added to 1.55 g (10 mmoles) ammonium salt of aci-CNA and then, 1 g (5 mmoles)

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