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A method of synthesis of fluorinated alkoxyethynyl ketones is described, by acylation of terminal acetylenic compounds with fluoracyl chlorides in the presence of CuCl.

<u>Keywords</u>: synthesis, fluorinated alkyoxyethynyl ketones, acylation, copper(I) chloride.

Fluorinated acetylenic ketones are useful synthons in organic synthesis. They have been obtained by the Grignard reaction [1]. Ethynyl ketones can be converted into amino-vinyl ketones,  $\beta$ -diketones, and  $\beta$ -diols which display many interesting and important properties [2].

Continuing work on the acylation of terminal acetylenic ketones by acyl chlorides in the presence of copper salts [3-5], which constitutes a more convenient method of obtaining acetylenic ketones, we have found that fluoroacyl chlorides react with acetylenic ethers in the presence of only stoichiometric amounts of Cu(I) chloride. The reaction proceeds in benzene in a stream of inert gas at 40-45°C, using triehtylamine as base.

$$\begin{array}{c} R^{1}COCI + R - C \equiv CH \xrightarrow{Cu(1)} R^{1} - CO - C \equiv CR \\ 1 & 2 \end{array}$$

$$R = (\overrightarrow{CH_{2}})_{5}CHOCH_{3}, R^{1} = CF_{3} (a); R = (CH_{3})_{2}COCH_{3}, R^{1} = CF_{3} (b). \end{array}$$

The presence in the IR spectra of the acetylenic ketones (2a-d) of absorption at 1720 (C=O) and 2220 cm<sup>-1</sup> (C=C), together with elemental analysis and GLC, confirm the purity and structures of the products.

## EXPERIMENTAL

IR spectra were obtained in CCl<sub>4</sub> on a UR-20 spectrometer, and GLC analyses carried out on a Khrom-4- chromatograph, column (360 cm  $\times$  0.4 cm) with 5% SE-30 on Inerton AW, carrier gas nitrogen.

The methyl ethers of the tertiary acetylenic alcohols (1), trifluoroacetyl and heptafluorobutyryl chlorides were obtained by standard methods [6-8].

 $\frac{4-(1 \text{ Methoxycyclohexyl})-1,1,1-\text{trifluorobut-3-yn-2-one (2a)}{2}.$  To a suspension of 20.0 g (0.2 mole) of CuCl in 150 ml of benzene was added 30.3 g (0.3 mole) of Et<sub>3</sub>N, the mixture stirred for 10 min in a stream of nitrogen, and 27.4 g (9.2 mole) of (1-methoxycyclohexyl)-acetylene (1a) added. Trifluoroacetyl chloride (27.8 g, 0.2 mole) was then introduced into the mixture by evaporation, and the mixture stirred at 40°C for 2 h. It was then treated with dilute HCl, washed with water, dried over MgSO<sub>4</sub>, evaporated, and distilled to give 26.5 g (56.6%) of (2a), bp 103°C (15 mm), nD<sup>21</sup> 1.4270. Found: C 56.88, H 5.54, F 24.69%. C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub>. Calculated: C 56.41, H 5.59, F 24.33%.

 $\frac{5-\text{Methyl-5-methoxy-1,1,1-trifluorohex-3-yn-2-one (2b)}{\text{g (0.2 mole) of 3-methyl-3-methoxybut-1-yne (1b), was 24.1 g (62.1%) of (2b), bp 62°C (42 mm), np<sup>21</sup> 1.3880. Found: C 49.80, H 4.75, F 28.92%. C<sub>8</sub>H<sub>9</sub>F<sub>3</sub>O<sub>2</sub>. Calculated: C 49.80, H 4.75, F 29.35%.$ 

Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 1, pp. 158-159, January, 1992. Original article submitted January 15, 1991.  $\frac{5-\text{Methyl-5-methoxy-1,1,1-trifluoroundec-3-yn-2-one (2c)}{\text{of 3-methyl-3-methoxynon-1-yne, yield 15.8 (59.8%), bp 61°C (1 mm), <math>n_D^{21}$  1.4120. Found: C 59.17, H 7.24, F 21.73%.  $C_{13}H_{19}F_{3}O_2$ . Calculated: C 59.08, H 7.24, F 21.56%.

 $\frac{1,1,1,2,2,3,3-\text{Heptafluoro-7-methyl-7-methoxytridec-5-yn-4-one (2d)}{\text{g (0.1 mole) of (1c) and 25.5 g (0.11 mole) of heptafluorobutyryl chloride, yield 18.9 g (51.9%), bp 93°C (5 mm) <math>n_D^{21}$  1.3920. Found: C 49.80, H 5.22, F 37.00%.  $C_{15}H_{19}F_7O_2$ . Calculated : C 49.45, H 5.25, F 36.5%.

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## METAL COMPLEX-CATALYZED SYNTHESIS OF DIHYDROTHIAPYRANS

FROM DIALKYL SULFOXIDES AND 1,3-DIENES

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A preparative method has been developed for the synthesis of dihydrothiapyrans from dialkyl sulfoxides and 1,3-dienes, catalyzed by palladium and nickel complexes. The scope of this reaction has been assessed, and a mechanism proposed, using 1,3-dienes and sulfoxides of varying structure.

<u>Keywords</u>: synthesis, dihydrothiapyrans, catalysts, mechanism, sulfides, 1,3dienes.

A frequently used method of synthesis of dihydrothiapyrans is by  $[2\pi + 4\pi]$ -cycloaddition of thioketones or thioaldehydes to 1,3-dienes [1, 2]. This method is of limited practical value since there are no convenient and efficient methods of preparation of the required thioaldehydes.

We have previously reported the one-step synthesis of dihydrothiapyrans by reacting dialkyl sulfoxides with 1,3-dienes in the presence of Pd and Ni complexes [3]. Under the reaction conditions, the sulfoxides break down to thioaldehydes which react with 1,3-dienes to give dihydrothiapyrans (DHTP). In order to obtain DHTP of varying structure, and to assess the range of applicability of this catalytic reaction of thioaldehydes generated in situ, we have examined the reactions of dialkyl and alkyl aryl sulfoxides with 1- and 2-substituted 1,3-dienes in the presence of catalytic complexes of Pd, Ni, Co, Cu, and Al which are effective catalysts for the reactions of conjugated dienes with sulfur-containing reagents [4].

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