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The system iodine — phenyl iodosoacetate (PIA) is a useful synthetic reagent in the conjugated iodoacetoxylation of ethylenic hydrocarbons in acetic acid solution [1] and of ketene in  $CCl_4$  solution [2]. The conjugated iodoacetoxylation of a double bond is regarded as the electrophilic addition of acetyl hypoiodide, which is formed by the following scheme:

$$C_6H_5I(OAc)_2 + I_2 \rightleftharpoons C_6H_5I + 2AcOI$$

It seemed of interest to study the reaction of alkynes with this system.

According to the data given in [3], acetyl hypoiodide, generated by the oxidation of iodine with peracetic acid, is capable of adding to the triple bond of tolan to give  $\alpha$ -iodo- $\beta$ -acetoxystilbene (IAS) in moderate yield, since this reaction is complicated by the parallel oxidation of the tolan to benzil. We found that disubstituted acetylenes react smoothly with iodine in the presence of PIA, when heated in acetic acid solution, to give in high yield the conjugated iodoacetoxylation products, and specifically  $\alpha$ -iodo- $\beta$ -acetoxyethylenes (I), which are not contaminated with  $\alpha$ -diketones.

$$R-C \equiv C-R \xrightarrow{I_{4} C_{6}H_{3}I(OAc)_{2}} R \xrightarrow{I OAc} R \xrightarrow{I OAc} R \xrightarrow{I_{4} C_{6}H_{3}I(OAc)_{2}} R = C_{6}H_{3}, n-C_{4}H_{9}$$

Attempts to add further to the double bond of (I) by using an excess of the reagents proved unsuccessful. The obtained iodoacetoxy derivatives are characterized by easy hydrolytic cleavage in either alkaline or acid medium: when heated with aqueous alcohol solution they give the corresponding  $\alpha$ -hydroxyketones in high yield, while the hydrolysis of IAS in the presence of HCl led to desyl chloride, which is probably formed via the step of forming the  $\alpha$ -iodoketone.

We did not study the stereochemistry of the iodoacetoxylation but did establish that the trans isomer is formed in the case of tolan, whose melting point and PMR spectrum are the same as those given in the literature for trans-IAS [3].

The above described reaction can have interest as a new method for going from alkynes to various carbonyl compounds.

## EXPERIMENTAL

The PMR spectra were taken on a Varian A-56/60A spectrometer (60 MHz) in  $CCl_4$  solution relative to HMDS, while the IR spectra were taken on a UR-20 instrument as KBr pellets.

 $\frac{\alpha - \text{Iodo} - \beta - \text{acetoxystilbene.}}{(0.025 \text{ mole}) \text{ of phenyl iodosoacetate in 15 ml of AcOH was refluxed for 0.5 h.}$  The precipitate obtained on cooling was filtered, washed with water, and recrystallized from alcohol to give 6.7 g (93%) of IAS, mp 144-145°C. Found: C 51.98; H 3.58; I 35.01%. C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>I. Calculated: C 52.75; H 3.57; I 34.89%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>); 1756 (C = O); 1208, 1230 (C - O). PMR spectrum ( $\delta$ , ppm): 1.78 s (CH<sub>3</sub>COO); 7.60 m (C<sub>6</sub>H<sub>5</sub>).

A solution of 10.9 g of IAS and 4 g of KOH in 50 ml of MeOH was refluxed for 2 h, diluted with water, and the precipitate was filtered and recrystallized from hexane to give 5.8 g (92%) of benzoin, mp 134-135° (mixed mp).

After refluxing 9.1 g of IAS in a mixture of 120 ml of 85% alcohol and 10 ml of HCl for 4 h the solution was poured into water, extracted with ether, and dried over MgSO<sub>4</sub>. After distilling off the solvent the residue

Institute of Petroleum Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Tomsk. Tomsk State Pedagogic Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5. pp. 1153-1154, May, 1978. Original article submitted June 10, 1977. was recrystallized from methanol to give 2.6 g (45%) of desyl chloride, mp 65-66° (mixed mp).

<u>5-Iodo-6-acetoxy-5-decene</u>. A solution of 6.44 g (0.02 mole) of PIA, 5.08 g (0.02 mole) of iodine, and 5.52 g (0.04 mole) of 5-decyne in 100 ml of AcOH was stirred for 2 h at ~20° and then let stand overnight. The mixture was diluted with water, the organic layer was separated, the aqueous layer was extracted with ether, and the combined extracts were washed in succession with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and water, dried over MgSO<sub>4</sub>, and the solvent was evaporated. The residue was chromatographed on a silica gel column to give 7.4 g (58%) of 5-iodo-6-acetoxy-5-decene (eluant = 1 :1 hexane - benzene), nD 1.4962. Found: C 44.37; H 6.20; I 39.31%. C<sub>12</sub>H<sub>21</sub>O<sub>2</sub>I. Calculated: C 44.50; H 6.48; I 39.20%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>, film): 1752 (C = O); 1210, 1240 (C - O).

A solution of 6.48 g of 5-iodo-6-acetoxy-5-decene and 4 g of KOH in 40 ml of MeOH was refluxed for 1 h, cooled, and poured into water. The organic layer was separated, the aqueous layer was extracted with ether, the combined extracts were dried over MgSO<sub>4</sub>, the solvent was removed, and the residue was vacuum-distilled to give 2.0 g (60%) of 5-hydroxy-6-decanone, bp 95-96° (1 mm);  $n_D^{20}$  1.4350 [4]. Found: C 70.00; H 11.60%.  $C_{10}H_{20}O_2$ . Calculated: C 69.76; H 11.63%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>, film): 1715 (C =O); 1208, 1240 (C - O).

## CONCLUSIONS

1. A simple method was proposed for the synthesis of  $\alpha$ -iodo- $\beta$ -acetoxyethylenes, which is based on the reaction of disubstituted alkynes with the iodine — phenyl iodosoacetate system.

2. The alkaline hydrolysis of the  $\alpha$ -iodo- $\beta$ -acetoxyethylenes leads to the corresponding  $\alpha$ -hydroxyke-tones.

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#### DIRECTION OF SUBSTITUTION IN IODINATION OF

# 5-HYDROXYPICOLINIC AND

## 3-HYDROXYISONICOTINIC ACIDS

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The iodination of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hydroxypyridinecarboxylic acids bears an ambiguous character. Depending on the reaction conditions and the structure of the hydroxypyridinecarboxylic acid, the substitution can proceed in two directions: without involving the COOH group or with the simultaneous decarboxylation and replacement of the COOH group by iodine. Thus, in [1-3] it was established that the 5-hydroxynicotinic, 5-hydroxypicolinic, and 3-hydroxyisonicotinic acids can be iodinated in the 6 position for the first two acids, and in the 2 position for the last acid, without involving the COOH group. The similar formation of the 3,5diiodo derivative by the halogenation of 4-hydroxynicotinic acid was mentioned in [4]. On the other hand, the iodination of the 3-, 5-, and 6-hydroxypicolinic acids under more drastic conditions proceeds with the simultaneous decarboxylation of the COOH group and the respective formation of the 2,6-diiodo-3-hydroxy- and 2,5diiodo-6-hydroxypyridines [5-7].

In this connection it seemed of interest to study the direction of the substitution in the iodination of the 5-hydroxypicolinic (I) and 3-hydroxypicotinic (II) acids as a function of the reaction conditions and type of

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