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HETEROCYCLIZATION REACTION OF PROPARGYL ACETATE WITH β-DICARBONYL COMPOUNDS

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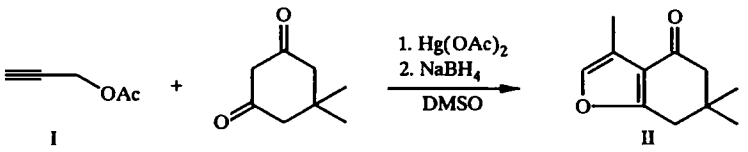
The regiochemistry of the reaction of propargyl acetate with CH acids in the presence of mercury(II) acetate in dimethylsulfoxide has been investigated. Derivatives of furan or unsaturated diketones were isolated depending on the nature of the 1,3-dicarbonyl and the possibility of reduction of the organomercury intermediate.

Methods have been developed for single stage functionalization of unsaturated compounds based on the mercuration-demercuration addition reaction [1-3]. We have also reported the reaction of amines, alcohols, carboxylic and CH acids with terminal acetylenes in the presence of mercury(II) acetate [4, 5]. In particular it has been shown that the addition of acetylacetone and ethyl acetoacetate to propargyl acetate (I) under electrophilic conditions with mercury(II) acetate led to the formation of linear vinylation products [5]. However, all our attempts to extend this reaction to dimedone under these conditions were unsuccessful. In contrast this reaction does occur in a polar solvent (DMSO) at 65°C. 3,6,6-Trimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (II) was isolated after demercuration of the intermediate with sodium tetrahydroborate.



I II

In a continuation of this valuable study we have investigated the reaction of propargyl acetate with acetylacetone and ethyl acetoacetate in a polar solvent. We demonstrated that when dimethylsulfoxide was used as the solvent and the organomercury intermediate was reduced with sodium tetrahydroborate the reaction (Scheme 1) unambiguously gave the cyclic products 3-acetyl-2,4-dimethyl- and 3-carbethoxy-2,4-dimethylfuran (XIa and XIb).

The formation of the furan derivatives XI in DMSO and their absence when the reaction was carried out in dioxane in all likelihood indicates the intermediate formation of compounds III, IV, and V, demercuration of which with sodium tetrahydroborate in an aqueous alkaline medium led to the diketone VII and the ketoenols VIII and IX respectively. Under these conditions the latter lose acetic acid and are converted into furan XI or are hydrolyzed into derivatives of the 1,4-diol XII. Compound XII in its turn may undergo intramolecular cyclization with loss of water to give furan derivatives. It should be noted that while the only reaction product is a furan derivative when the intermediate organomercury compound is reduced with sodium tetrahydroborate, a prototropic equilibrium was observed on protolysis of the C-Hg bond with hydrochloric acid, in consequence of which the acetoxy-substituted unsaturated β-diketones X are formed, hydrolysis of which led to the unsaturated diketoalcohols XIII. The presence of cyclic products when the mixture is treated with hydrochloric acid is explained by conversion of some of the intermediate products IV and V, which exist in the enol form no matter whether the reagent is sodium tetrahydroborate or hydrochloric acid, undergo intramolecular cyclization. In fact this shows that the linear products with an exomethylene structure obtained by the reaction of propargyl acetate with acetylacetone in dioxane [5] are converted into the furans XI by intramolecular cyclization when mercury(II) acetate is used as the mercurating agent in dimethylsulfoxide

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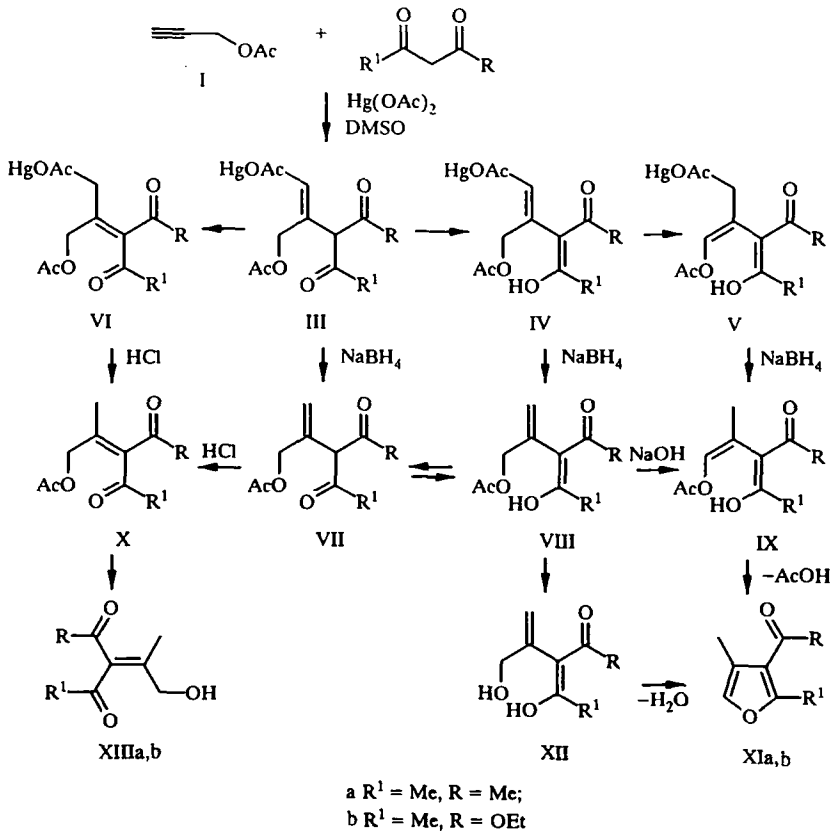
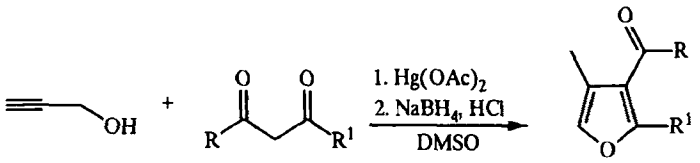
Scheme 1



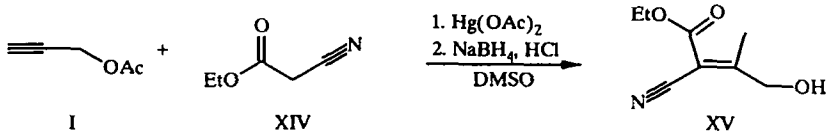
a R^1 = Me, R = Me;
b R^1 = Me, R = OEt

under the conditions described in [6]. The isolation of furans during the reaction with 1,4-diols confirmed the suggestion that enols are necessary for intramolecular cyclization. The results of the reactions of propargyl alcohol with CH acids to give small yields (10-15%) of the furan derivatives II and XI is in agreement with this.



II R + R^1 = $CH_2CMe_2CH_2$

Propargyl acetate did not react with ethyl cyanoacetate (XIV) in dioxane, but the addition reaction was successful in DMSO to give the unsaturated ketoalcohol XV, no matter what the reduction conditions, which indirectly confirms the suggestion that the enol form is necessary for intramolecular cyclization to occur:



EXPERIMENTAL

IR spectra were recorded with a UR-20 instrument. ^1H NMR Spectra were recorded with a Perkin-Elmer R-12B spectrometer (60 MHz, CCl_4) and GLC was carried out with an LKM-80 apparatus with a thermal conductivity detector, a

TABLE 1. Physicochemical Characteristics of the Furan Derivatives II, XIa and b and the Ketoalcohols XIIIa, b, and XIV

Compound	Molecular formula	(Found, %) / (Calculated, %) C	H	N	Time, h	bp, °C (mm Hg)	IR spectrum (ν, cm^{-1})	^1H NMR spectrum (CCl_4), δ, ppm (J, Hz)	Yield, %
II	$C_{11}H_{14}O_2$	75,1 / 74,2	7,8 / 7,3	–	24	110(5)	1560, 1600, 1680	1,09 s (6H, CH_3), 2,13 s (2H, CH_2), 2,24 s (3H, $-CCH_3$), 2,67 s (2H, CH_2), 7,07 s (1H, CH)	28,1
XIa*	$C_8H_{10}O_2$	70,2 / 69,6	7,4 / 7,2	–	48	83(11)	1560, 1590, 1660	2,11 s (3H, $-CCH_3$), 2,29 s (3H, $COCH_3$), 2,49 s (3H, CH_3), 6,93 s (1H, CH)	43,5
XIb*	$C_9H_{12}O_3$	64,6 / 64,3	7,8 / 7,1	–	48	85(15)	1580, 1620, 1720	1,31 t (3H, OCH_2CH_3), 2,07 s (3H, $COCH_3$), 2,47 s (3H, CH_3), 4,22 q (4H, OCH_2CH_3), 7,02 s (1H, CH)	36,9
XIIIa	$C_8H_{12}O_3$	61,9 / 61,5	7,5 / 7,7	–	48	88(12)	1665, 1720, 3610	2,0 s (3H, $-CCH_3$), 2,09 s (6H, $COCH_3$), 3,46 s (2H, CH_3), 7,91 s (1H, OH)	22,1
XIIIb	$C_9H_{14}O_4$	59,9 / 58,1	8,8 / 7,5	–	48	93(16)	1650, 1720, 3610, 1740	1,3 t (3H, OCH_2CH_3), 1,95 s (3H, $-CCH_3$), 2,09 s (3H, $COCH_3$), 3,29 s (2H, CH_2OH), 4,09 q (2H, OCH_2CH_3), 7,81 s (1H, OH)	10,5
XV	$C_8H_{11}O_3N$	57,4 / 56,8	7,3 / 6,5	8,5 / 8,3	48	106(25)	1680, 1750, 2280, 3560	1,3 t (3H, OCH_2CH_3), 1,82 s (3H, $-CCH_3$), 3,6 s (2H, CH_2OH), 4,26 q (2H, OCH_2CH_3), 7,78 s (1H, OH)	72

*Physicochemical characteristics identical to literature data [7].

2000 × 3 mm column with 5% SE-30 on Chromaton N-AWDMCS (0.16-0.2 mm) as stationary phase, temperature from 150-180°C, and helium carrier gas (40 ml/min).

Reaction of Propargyl Acetate with CH Acids. Mercury (II) acetate (0.025 mol) was dissolved in DMSO (50 ml), propargyl acetate (0.05 mol) was slowly added, the mixture stirred for 1 after which the sodium salt of the CH acid (0.05 mol) in DMSO (100 ml) was added and the mixture was heated to 65°C (heating time is given in Table 1). The decomposition of the organomercurial was carried out in two ways.

Method A. Sodium tetrahydroborate (0.04 mol) was added in portions, stirred for 2 h and poured into a 1:2 ether–water mixture. The organic substance was extracted with ether and the product was distilled in vacuum. Yields of furans XIa 85%, XIb 78%.

Method B. Hydrochloric acid (60 ml) was added to the reaction mixture, stirred for 2 h, and extracted with ether. The reaction products were distilled in vacuum. The yields and physicochemical characteristics of the products are cited in Table 1.

Reaction of Propargyl Alcohol with CH-Acids. Mercury(II) acetate (0.025 mol) was dissolved DMSO (50 ml), propargyl alcohol (0.05 mol) was added slowly, the mixture was stirred for 1 h, after which the sodium salt of a CH acid (0.05 mol) in DMSO (80 ml) was added and the mixture was heated to 65°C (heating time is given in Table 1). Hydrochloric acid (60 ml) was added to the reaction mixture which was stirred for 2 h and extracted with ether. The product was distilled in vacuum.

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