CARBONYLATION OF ACETYLENIC COMPOUNDS.

1. CARBONYLATION OF TERTIARY ACETYLENIC ALCOHOLS

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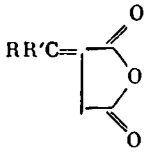
Alkyl- and alkenylsuccinic acids and their derivatives are used in the preparation of many practically important products [1], which is one of the reasons for the increasing interest in the synthesis of these compounds [2-5]. Among the recently proposed methods for the synthesis of alkyl- and alkenylsuccinic acids and their derivatives, the method of the $PdCl_2$-catalyzed carbonylation of propargyl alcohols (100°C, CO at 100 atm) [5] is very promising:

$$\underset{(I)}{RR'C(OH)C{\equiv}CH} + CO + H_2O \rightarrow [RR'C{=}C{=}CHCOOH] \xrightarrow{CO+H_2O}$$

$$\rightarrow \underset{(II)}{RR'C{=}C(COOH)CH_2COOH} \rightarrow$$



Together with the convenient method for the preparation of acetylenic carbinols developed by us [6], this reaction (if carried out under milder conditions, eliminating the danger of strong resinification of higher acetylenic alcohols) can considerably widen the possibilities of the synthesis of the above compounds. In the present work we searched for a more effective catalyst, so that it would be possible to lower the temperature and pressure, and studied the carbonylation of propyn-2-ol (Ia), 2-methyl-3-butyn-2-ol (Ib), 1-ethynylcyclopentanol (Ic), and 2-phenyl-3-butyn-2-ol (Id) in the presence of Pd-black and HI in solutions of benzene and MeOH [7].

During the carbonylation in a benzene solution, alcohol (Ia) actively adds CO, but the products formed cannot be isolated because of rapid polymerization. Alcohols (Ib-d) form substituted anhydrides of succinic acid (IIIb-d). The reaction thus takes place under milder conditions than in the presence of $PdCl_2$ [5] (Table 1).

When boiled with water, anhydrides (III) convert into acids (II).

The carbonylation of (I) in MeOH leads to a mixture of products, which is due to the concurrent substitution of the OH group for MeO. Thus, during the carbonylation of alcohol (Ia), a mixture of dimethyl itaconate (IV) and dimethyl aconitate (V) is formed in a ratio of 6:1 (overall yield 35%):

$$\underset{(Ia)}{HC{\equiv}CCH_2OH} \xrightarrow[-H_2O]{CO+MeOH} [CH_2{=}C{=}CHCO_2CH_3] \xrightarrow{CO+MeOH} \underset{(IV)}{CH_2{=}C(CO_2CH_3)CH_2CO_2CH_3}$$

$$\xrightarrow[-H_2O]{CO+MeOH} [CH_3O_2CCH{=}C(CO_2CH_3)CH_2OCH_3] \rightarrow$$

$$\xrightarrow{CO} \underset{(V)}{CH_3CO_2CH{=}C(CO_2CH_3)CH_2CO_2CH_3}$$

From (Ib), together with the diester (VI), the methoxy-substituted compounds (VII) and (VIII), as well as the lactone (IX) are formed. Further carbonylation of (VII) and (VIII) is apparently hindered by the methyl substituents in the α position to the MeO group (see scheme on following page). All the products were isolated by chromatography on a SiO_2 column, and characterized (Tables 2 and 3).

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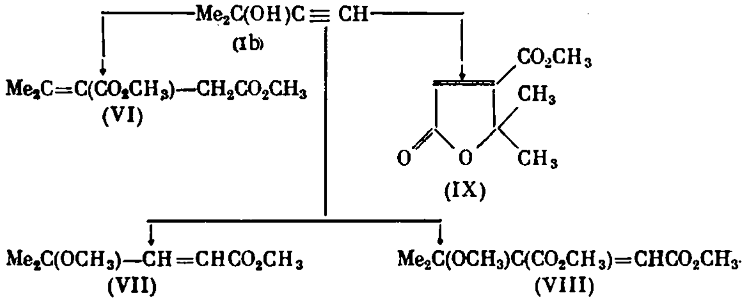
TABLE 1. Carbonylation of Propyn-2-ol (Ia), 2-Methyl-3-butyn-2-ol (Ib), 1-Ethynylcyclopentanol (Ic), and 2-Phenyl-3-butyn-2-01 (Id) in the Presence of Pd-Black and HI in Benzene

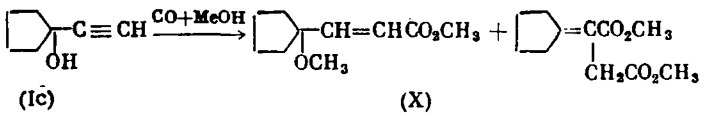
Alcohol	Temperature of reaction, °C	CO pressure, atm	Time, h	Product, yield, %
(Ia)	30	20	1,5	Resin
(Ib)	60	20	3	(IIIb),, 45
(Ic)	70	50	5	(IIIc),, 36
(Id)	30	50	2	(IIId),, 51

TABLE 2. Products of Saponification of Anhydrides (IIIb-d)

Anhydride	Acid	mp, °C (solvent)	UV spectrum		IR spectrum ν, cm^{-1}	PMR spectrum, ppm	Empirical formula	Found/Calculated %	
			λ_{max}, nm	ε				C	H
(III b)	(II b)	162–163 (EtOH)	235	12400	1620, 1655	—	—	—	—
(III c)	(II c)	220–221 (EtOH)	242	12650	1630, 1660, 1710	1,80, 2,40, 2,76 $(CH_2)_4$, 3,26 (CH_2), 9,23 (COOH)	$C_9H_{12}O_4$	58,76/58,69	6,58/6,57
(III d)	(II d)	161–162 (MeOH)	208	15100	1630, 1660, 1710	2,36 (CH_3), 3,11 (CH_2), 7,26 м (C_6H_5), 9,06 (COOH)	$C_{12}H_{12}O_4$	65,92/65,44	5,52/5,42



Carbonylation of (Ic) leads to a mixture of methoxy-monoester (X) and diester (XI)



(XI)

In this case, the products of the cis-carbonylation of the C ≡C bond are not formed, probably because of steric hindrances. All the reactions in MeOH are also carried out under mild conditions (20-50 atm, 40-70°C, 2-4 h).

Palladium black was thus found to be an active catalyst for the carbonylation of acetylenic alcohols and the synthesis of succinic acid derivatives. However, only Pd-black which shows pyrophoric properties is effective, but this cannot always be prepared, and even under mild conditions, the reaction takes place with considerable resinification.

In continuation of our search for carbonylation catalysts for acetylenic alcohols, we studied the catalytic activity of a homogeneous catalyst $Co_2(CO)_8$. This catalyst has not yet been used for carbonylation of acetylenic alcohols, but was used in the reaction of CO with acetylene, and one of the products of this reaction was succinic acid [8]. It is also known that nickel carbonyls catalyze the carbonylation of acetylenic alcohols to unsaturated acids only [9].

We studied the catalytic activity of $Co_2(CO)_8$, using different additives in the case of (Ib). The results are listed in Table 4. The principal reaction products are teraconic an-

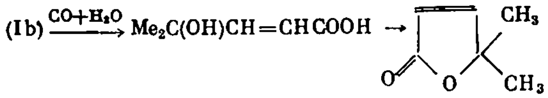
TABLE 3. Products of Carbonylation of Alcohols (Ia-d) in Presence of Pd-Black

Alcohol	Reaction conditions: solvent; T, °C; P, atm; time, h	Carbonylation product	Yield, %	bp, °C (P, mm Hg) mp, °C (solvent)	n_D^{20}	IR spectrum ν, cm⁻¹	PMR spectrum, ppm, J, Hz	Empirical formula	Found/Calculated, % C	Found/Calculated, % H
(Ia)	MeOH; 40; 20; 3	(IV) cf. [5]	30	93–95(10)	1,4440	1660, 1730	3,23(CH_2), 3,61, 3,70(CO_2CH_3), 5,66, 6,20(=CH)			
		(V) cf. [5]	5	80–81(25)	1,4660	1660, 1730	3,63, 3,71, 3,78(CO_2CH_3), 3,85(CH_2), 6,83(CH=)			
(Ib)	C_6H_6; 50; 20; 3	(IIb) cf. [5]	45	104–105(0,5) 42–43(EtOH)		1680, 1770, 1840	1,9(CH_3), 2,24(CH_3), 3,34(CH_2)			
		(VI) cf. [5]	18	72–73(7)	1,4440	1075, 1660, 1730	1,26(CH_3), 3,13(OCH_3), 3,65(CO_2CH_3), 5,90, 6,80(CH=CH, J=16)			
(Ib)	MeOH; 50; 50; 3	(VII) cf. [5]	10	100–101(7)	1,4718	1640, 1740	1,78, 2,07(CH_3), 3,22(CH_2), 3,56, 3,60(CO_2CH_3)			
		(VIII) cf. [5]	0,8	99–100(0,7)	1,4612	1070, 1650, 1735	1,3(CH_3), 3,11(OCH_3), 3,60, 3,70($COCH_3$), 5,80(CH=)			
		(IX)	0,6	79–80(0,7)	1,4820	1740, 1765	1,33(CH_3), 3,66(CO_2CH_3), 6,43(CH=)	$C_8H_{10}O_4$	56,30 56,46	6,08 5,92
(Ic)	C_6H_6; 70; 50; 5	(IIc)	36	149–150(0,7) 51–52(EtOH)		1680, 1770, 1840	1,80, 2,30, 2,80$(CH_2)_4$, 3,29(CH_2)	$C_9H_{10}O_3$	64,85 65,05	6,09 6,07
		(X)	20	63–64(0,7)	1,4750	1070, 1660, 1725	1,70$(CH_2)_4$, 3,10(OCH_3), 3,60(CO_2CH_3), 5,80(CH=, J=16), 6,83(=$CHCO_2$)	$C_{10}H_{16}O_3$	64,17 64,19	8,74 8,75
(Ic)	MeOH; 70; 50; 5	(XI)	30,5	96–97(0,7)	1,4864	1650, 1720, 1740	1,76, 2,35, 2,76$(CH_2)_4$, 3,21(CH_2)	$C_{11}H_{16}O_4$	62,10 62,25	5,14 4,99
(Id)	C_6H_6; 30; 50; 2	(IId)	51	140–141(0,5) 106–107(C_6H_6)		1500, 1630, 1770, 1830	2,5(CH_3), 3,02(CH_2), 7,20(C_6H_5)	$C_{12}H_{10}O_3$	71,41 71,28	5,14 4,99

TABLE 4. Carbonylation of (Ib) in Presence of $Co_2(CO)_8$ with Different Additives (150°C, CO at 100 atm)

Catalyst	Overall yield of (IIb), (VII), and (XII), %	Relative yield, %		
		(IIб)	(VII)	(XII)
$Co_2(CO)_8$+HI+CH_3OH	53,4	42,1	50,4	7,5
$Co_2(CO)_8$+HI+Py+CH_3OH	49,2	25,6	32,3	42,1
$Co_2(CO)_8$+C_6H_6	15,3	–	–	100
80,7% CoNa(SiO_2/Al_2O_3=4,4)	58,3	28,8	47,9	23,3

hydride (IIb) and diester (VI). 5,5-Dimethyl-$\Delta^{3,4}$-dihydrofuran-2-one (XII) is also formed in a small amount


$(Ib) \xrightarrow{CO+H_2O} Me_2C(OH)CH{=}CHCOOH \rightarrow$

(XII)

EXPERIMENTAL

The PMR spectra were run on the Varian DA-60-IL spectrophotometer (60 MHz). The chemical shifts are shown on a δ scale, using HMDS as standard and $CDCl_3$ as solvent. The IR spectra were recorded on the UR-10 spectrometer, and the UV spectra on the Specord UV-VIS apparatus. The products were analyzed by TLC (on Silufol) and by GLC (2.5 m × 3 mm column with 2.5% OV-1 on Chromosorb G, 80-100 mesh).

Carbonylation in the Presence of Pd-Black. A 0.25-mole portion of the acetylenic alcohol (I), 100 ml of solvent, 0.3 g of Pd-black, and 3 g of 40% HI were placed in a thermostated stainless-steel reactor with mechanical stirring, and then CO was introduced to a pressure of 20 atm. The mixture was heated until no more CO was absorbed. During the absorption, more CO was added. The catalyst was filtered, the reaction mixture was passed through a column with SiO_2 to purify it from resins, and the solvent was distilled. The products were isolated by fractional distillation, and the mixtures were separated by column chromatography (SiO_2, ether–hexane, 1:1) (see Table 3).

Carbonylation in the Presence of $Co_2(CO)_8$. In a rotating 0.25-liter steel autoclave were placed 42.2 g (0.5 mole) of (Ib), 32 ml of methanol, a solution of 1.2 g of $Co_2(CO)_8$ in 25 ml of hexane, and 5 ml of 40% HI. The autoclave was heated, with rotation, to 150°C at a CO pressure of 100 atm. The CO absorption was continued for 6 h. The reaction mixture was washed with 10% HCl, a saturated solution of NaCl, and water, and dried over Na_2SO_4. The products were isolated by fractional distillation and column chromatography (SiO_2, ether–petroleum ether, 1:1), to yield 17.7 g (25.3%) of (IIb), 21 g (22.6%) of (VII), and 3.1 g (5.5%) of (XII), bp 70-71°C (7 mm), n_D^{20} 1.4466. PMR spectrum (δ, ppm): 1.42 (CH_3), 5.80, 7.36 (CH =CH, J =16 Hz). Found: C 64.12; H 7.14%. $C_6H_8O_2$. Calculated: C 64.27; H 7.19%.

CONCLUSIONS

Carbonylation of acetylenic alcohols in the presence of Pd-black and cobalt carbonyl leads to derivatives of alkylidenesuccinic acids in yield of ~50%.

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REACTION OF ETHYL DIAZOACETATE WITH 2-ALKENYLFURANS*

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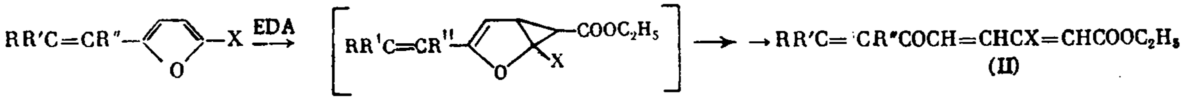
In contrast to benzene, furan and its derivatives react with ethyl diazoacetate (EDA) under conditions of thermocatalytic decomposition of the latter with the formation of complexes of the ethoxycarbonylcarbene fragment at the double bond of the furan ring (FR) and products of their rearrangement [6, 7], which indicates the great activity of the FR compared to benzene in these reactions. The possibility of competition between the multiple bonds of FR and of the alkenyl group emerges in the case of alkenylfurans. In connection with this we studied the influence of a substituent in position 5 of the FR and at the exocyclic double bond of 2-alkenylfurans (I), and also the influence of the conditions of the process on the direction of the reaction and the relative activity of the exocyclic and endocyclic double bonds of (I) in comparison to EDA.

As was shown, the reaction of EDA with (I), having substituents on the vinyl group [2-propenylfuran (Ia), 2-isobutenylfuran (Ib), 2-(1,2-dimethylvinyl)furan (Ic)], leads mainly to acyclic esters of triene ketoacids (II), with yields in the case of the thermocatalytic reaction in the presence of $CuSO_4$ reaching 47-58%:



(I)

$R=CH_3$, $R'=R''=X=H$ (a); $R=R'=CH_3$, $R=X=H$ (b);
$R=R''=CH_3$, $R'=X=H$ (c); $R=R'=X=CH_3$, $R''=H$ (d);
$R=R'=R''=X=H$ (e); $R=R'=R''=H$, $X=CH_3$ (f).

The formation of (II) can be explained by participation in the reaction of the double bond of FR, removed from the alkenyl substituent, with subsequent rearrangement of the complex [6, 7]. The absence of addition products of carbene at the substituted bouble bond of FR is

TABLE 1. Properties of Esters of Triene Ketoacids $RCO(CH=CH)_2COOC_2H_5$ (II)

Classification number	R	mp, °C	Found			Empirical formula	Calculated		
			C, %	H, %	M^+/e		C, %	H, %	mol. wt.
(IIa)	$CH_3CH=CH$	83	67,94	7,18	194	$C_{11}H_{14}O_3$	68,02	7,26	194,2
(IIb)	$(CH_3)_2C=CH$	84	68,47	7,76	208	$C_{12}H_{16}O_3$	68,82	8,25	208,2
(IIc)	$CH_3CH=C(CH_3)$	92	68,81	8,15	208	$C_{12}H_{16}O_3$	68,82	8,25	208,2

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*The preliminary results are presented in [1, 2]; see also [3-5].

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