

# HYDROGENOLYSIS OF SYMMETRICALLY SUBSTITUTED 2-BUTYNE-1,4-DIOL ESTERS

By

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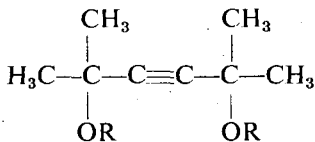
(Received September 1, 1972)

The hydrogenolysis of some 2-butyne-1,4-diol esters was examined at ordinary temperature and pressure in the presence of Adams  $\text{PtO}_2$  catalyst. The hydrogenation curves were recorded and the hydrogenolysis process was followed by titration of aliquots drawn at regular intervals. It was found that hydrogenation and hydrogenolytic processes run parallel and hydrogenolytic cleavage occurs mainly with the olefin intermediary products. Both rate and extent of the reactions are strongly influenced by the steric requirements of the substituents.

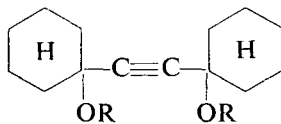
The low-pressure hydrogenation of 2-butyne-1,4-diol esters to the corresponding olefin and paraffin diol esters was extensively studied by ZAL'KIND, GVERDSITELI and MIKADZE [1—3]. They found that the hydrogenation reaction proceeded at different rates, in accordance with the activity of the various catalysts employed, and that in case of low activity catalysts the reaction stopped after consumption of one mole hydrogen to give an olefin derivative. Moreover, the rate of hydrogenation depended upon the structure both of the diol and the carboxylic acid acylating the hydroxylic groups. Obviously, the pressure of hydrogen and the reaction temperature, too, considerably affected the reaction.

In some cases, the hydrogenolysis of the ester bond was also observed to accompany the hydrogenation reaction [4]. However, the phenomenon has neither been examined systematically, nor quantitative relationships have been revealed.

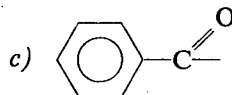
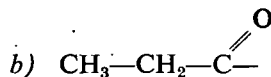
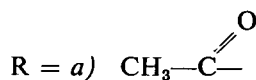
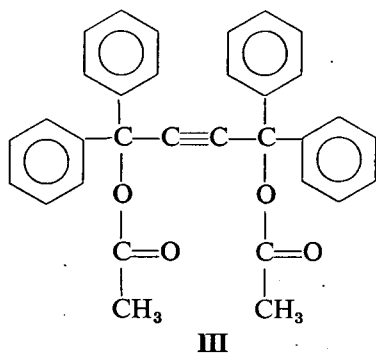
As a continuation of our earlier examinations [5, 6], we have prepared some 2-butyne-1,4-diol esters (I—III) and studied their hydrogenolysis at ordinary temperature and pressure, using platinum catalyst.



I



II



The choice of the model compounds was made so as to permit a study of the influence of the substituents attached to the hydroxyl-bearing carbon atoms and the esterifying carboxylic acids, as well.

#### *Method and apparatus*

The experiments were carried out in the hydrogenation vessel shown in Fig. 1, which was connected to a 1 l. gas-burette. Hydrogenations were conducted at atmospheric pressure and room temperature ( $23 \pm 2^\circ\text{C}$ ); the hydrogenation vessel was shaken at a frequency of 70/min.

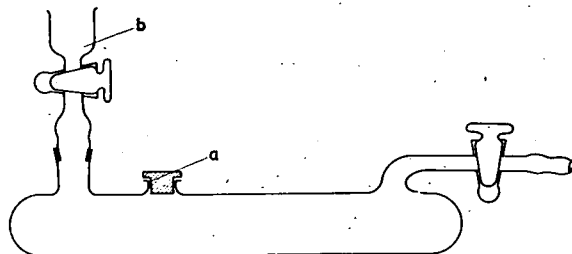


Fig. 1

Two series of measurements were carried out:

- a) the hydrogenation curves were drawn
- b) the rate of formation of the carboxylic acid component, released during hydrogenation by hydrogenolysis, was determined.

In drawing the hydrogenation curves, the catalyst was pre-hydrogenated in abs. ethanol and the previously dissolved model compound was added, with careful exclusion of air, to the hydrogenation vessel through cup *b* in Fig. 1. Shaking was immediately started, the consumption of hydrogen was read in 5 minute intervals and the results were plotted against time (Fig. 2).

The hydrogenolysis of the ester bond, *i.e.* the rate of formation of the carboxylic acid component released during this process, was followed by drawing samples

from the reaction mixture at regular intervals. The experimental conditions and the preparatory manipulations were identical in all respects with those detailed in the foregoing. Samples were drawn in 15 minute intervals with a hypodermic needle through hole *a* in Fig. 1, closed with a rubber stopper. The samples were immediately titrated with 0.01 *N* sodium hydroxide standard solution using phenolphthalein indicator and the consumption of the alkaline standard solution was plotted against time (Fig. 3).

### Results and discussion

Under the experimental conditions employed, only compounds Ia, Ib, IIa and IIb of the model compounds prepared for the purpose of the recent investigations could be induced to take up hydrogen. Since the equilibrium constant for dissociation of the carboxylic acids establishing the ester bonds in our model compounds, and consequently the stability constants of these ester bonds differed only to an almost negligible extent (Table I), the difference might alter the rate and extent of hydrogen uptake, respectively, to a small extent only [7].

This factor alone can by no means explain the failure of the reaction.

The failure of the hydrogenation reaction in the cases of tetraphenyl-2-butyne-1,4-diol diacetate (III) and the two dibenzoates (Ic and IIc) must be attributed to steric reasons. Evidently, the bulky phenyl groups prevent the approach of the molecules to the active sites of the catalyst to an effective closeness and owing this circumstance the hydrogenation reaction does not proceed.

The smooth pattern of the hydrogenation curves with a shape characteristic of saturation processes (Fig. 2) indicates that the esters take up the first two moles of hydrogen at a high rate and that the hydrogen consumption reactions do not proceed successively, stepwise, but simultaneously. In case of the dipropionate esters (Ib, IIb), the curves are similar to those of the acetate esters (Ia, IIa), but both the rate and the extent of hydrogen uptake are lower. The same difference appears in comparing the corresponding esters of tetramethyl-2-butyne-1,4-diol and bis-(1-hydroxycyclohexyl)acetylene (Ia, Ib, and IIa, IIb), respectively. The decrease in reactivity is explained in both cases with the greater space requirement of the propionyl and the cyclohexyl groups, respectively, giving rise to steric hindrance.

Table I  
Equilibrium constants for dissociation of the acids

Acid	pK <sub>a</sub>
Acetic	4.76
Propionic	4.87
Benzoic	4.20

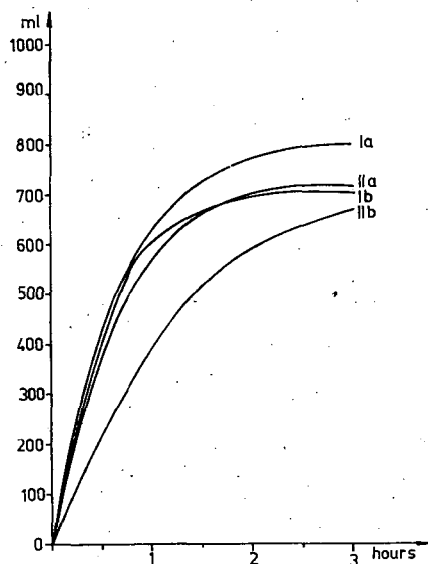


Fig. 2

Examination of the acidity—time curves (Fig. 3), *i.e.* the alkaline standard solution consumed by aliquot samples *vs.* time, reveals that hydrogenolysis, *i.e.* formation of carboxylic acids, begins immediately upon starting the hydrogenation. The smooth, unbroken shape of the curves supports also here the simultaneity of the reactions. The extent of hydrogenolysis, in accordance with that observed with the hydrogenation curves, decreased with increasing steric hindrance in this case, too.

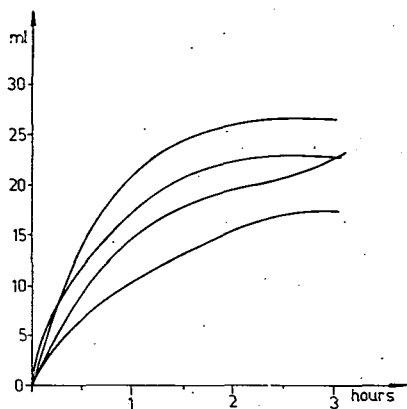


Fig. 3

Since the formation of carboxylic acids ran to a considerable extent (0.2—0.6 equivalent) already during consumption of the first mole of hydrogen (10—30 min), it must be assumed that hydrogenolytic cleavage of the ester bond occurs both in the olefin and the acetylene forms of the molecules. This is in accordance with the results obtained in the hydrogenation of 2-butyne-1,4-diols [8], though with these diols hydrogenation proceeded to a lesser extent. Taking into consideration that addition of hydrogen to the acetylene bond proceeds rather fast under the conditions applied, the hydrogenolytic process must run predominantly with the olefin intermediates of hydrogenation, since

hydrogenolysis of the corresponding paraffin derivatives is unlikely.

Considering the extent of hydrogenolysis (Fig. 4), the conclusion may be drawn that cleavage of only one of the ester bonds in the molecule is favoured and consequently

Table II

Physical constants and rate of hydrogenolysis

Compound	No.	Formula (Mol. wt.)	M.p., °C (B.p., °C)	N/100 NaOH ml	Hydro- geno- lysis, %
Tetramethyl-2-butyne-1,4-diol diacetate	Ia	C <sub>12</sub> H <sub>18</sub> O <sub>4</sub> (226.27)	24 (78/3 torr)	25.5	64
Tetramethyl-2-butyne-1,4-diol dipropionate	Ib	C <sub>14</sub> H <sub>22</sub> O <sub>4</sub> (254.33)	(88—90/4 torr)	21.9	55
Tetramethyl-2-butyne-1,4-diol dibenzoate	Ic	C <sub>22</sub> H <sub>22</sub> O <sub>4</sub> (350.48)	116	—	—
Bis-(1-hydroxycyclohexyl)-acetylene diacetate	IIa	C <sub>18</sub> H <sub>26</sub> O <sub>4</sub> (306.41)	46 (106—8/5 torr)	22.6	57
Bis-(1-hydroxycyclohexyl)-acetylene dipropionate	IIb	C <sub>20</sub> H <sub>30</sub> O <sub>4</sub> (334.46)	(156/3 torr)	17.8	45
Bis-(1-hydroxycyclohexyl)-acetylene dibenzoate	IIc	C <sub>28</sub> H <sub>30</sub> O <sub>4</sub> (430.55)	115	—	—
Tetraphenyl-2-butyne-1,4-diol diacetate	III	C <sub>30</sub> H <sub>26</sub> O <sub>4</sub> (450.54)	168—170	—	—

the product mixture consists mainly of the ester (IX) of the saturated monohydroxy derivative.

Taking into account the hydrogenation—hydrogenolytic processes of the examined model compounds (IV—XV) possible in principle and the above discussion, the most probable reaction pathways of the hydrogenation—hydrogenolysis of 2-butyne-1,4-diol esters are those indicated by full arrows in the reaction scheme.

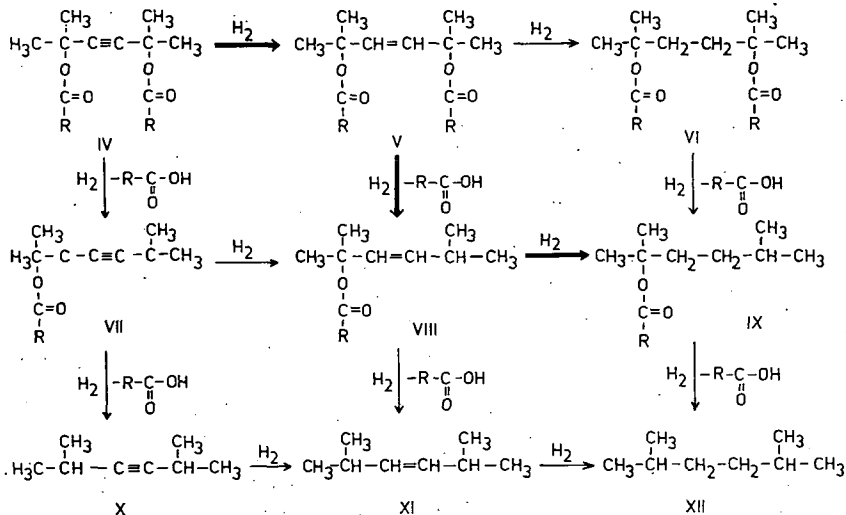


Fig. 4

Determination of the relative rates of hydrogenolytic processes in the acetylene and the corresponding olefin derivatives requires further experiments.

### Experimental

All melting points were determined by a Kofler micro hot stage and the values given are corrected. Before the analysis, the samples were dried for 12 hours over phosphorus pentoxide. The infrared spectra were recorded by a Unicam SP 200 spectrophotometer.

The diols used in the preparation of the model esters were obtained by our method described earlier [6], while esterification was achieved by standard procedures. The Adams  $\text{PtO}_2$  catalyst was prepared from ammonium chloroplatinate.

### General hydrogenation procedure

0.1 g Adams  $\text{PtO}_2$  catalyst was placed in the hydrogenation vessel (Fig. 1) and covered with 20 ml abs. ethanol. Air was removed from the apparatus by flushing with hydrogen and the catalyst was prehydrogenated (3 hours). Then a solution

of 0.01 mole ester in 80 ml abs. ethanol was added to the catalyst, the shaking immediately started and the hydrogen consumption read at intervals of 5 minutes.

In drawing the samples the preparation was done similarly in all respects to that described in the foregoing, samples were taken in 15 minute intervals and titrated.

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The authors thank to Mr. A. GAJDACSI for technical assistance, Drs. K. L. LÁNG and G. B. BOZÓKI for the microanalyses and for recording the spectra.

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#### ГИДРОГЕНОЛИЗ СЛОЖНЫХ ЭФИРОВ РАЗЛИЧНЫХ СИММЕТРИЧНЫХ 2-БУТИН-1,4-ДИОЛОВ

*П. М. Агоч и К. Кoczka*

Изучен гидрогенолиз некоторых эфиров ацетилен-1,4-диолов при атмосферном давлении и комнатной температуре в присутствии  $PtO_2$  катализатора Адамса. Определены кривые прохождения гидрогенизации и на основании взятых проб найдена кинетика гидрогенолиза. Показано, что реакции гидрогенизации и гидрогенолиза проходят одновременно и большая доля гидрогенолитических отщеплений происходит в состоянии олефинов. Развитие реакций и их скорость в значительной мере зависит от объема заместителей.