SYNTHESIS AND PYROLYSIS OF ACETOACETIC AND (ETHOXYCARBONYL)ACETIC ESTERS OF α-ETHYNYL- AND α-VINYL-3-CYCLOHEXENE-1-METHANOLS

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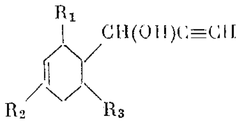
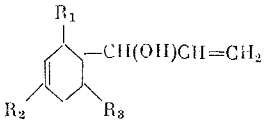
Carrol's reaction [1-4], which has been well studied for tertiary acetylenic and ethylenic alcohols, has found fairly wide application in the synthesis of polyenic compounds [5]. However, the participation of secondary alcohols in this reaction has received little investigation. There are a few references in the literature [2-4, 6] according to which unsaturated ketones have been obtained in yields of 12-88% from secondary ethylenic alcohols of the aliphatic series, but from secondary acetylenic alcohols the corresponding ketones are not formed at all [7]. It has also been shown that some secondary acetylenic alcohols do not react with 2-acetylacetoacetic ester [8].

At the start of our investigations there were no data at all on the participation of unsaturated alcohols derived from 3-cyclohexene-1-methanol of types A and B in the Carrol reaction.



A



B

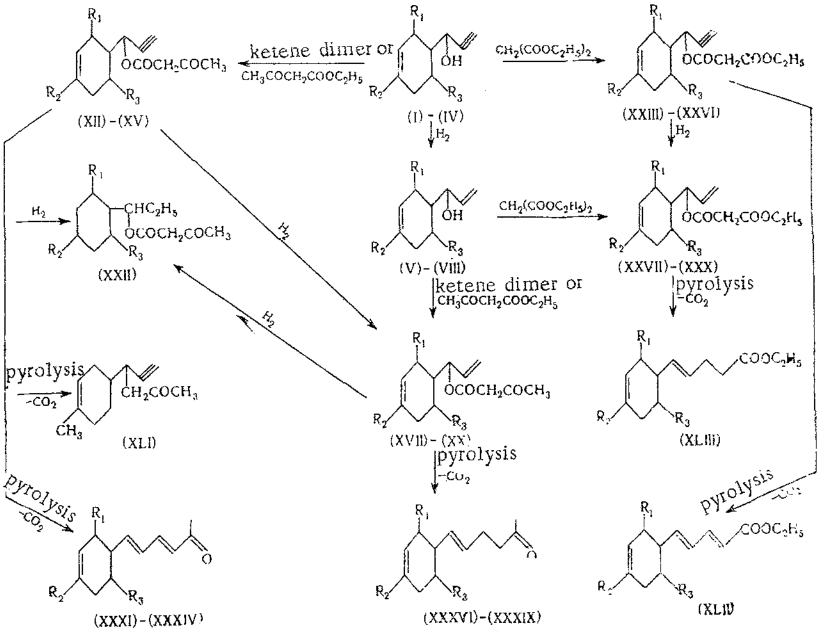
R_1, R_2, R_3=H or CH_3

On the basis of the already available experimental data [9] it could, however, be supposed that in the course of the formation of trienones from alcohols of type A the isomerization of the Δ^3 bond into the Δ^6 position could occur. Hence, the possibility of using these alcohols for the synthesis of unsaturated ketones and acids by the Carrol method could open up easy routes to the preparation of natural cycloaliphatic polyenes and their analogs containing the double bond in the 6-position of the ring.

For the study of the Carrol reaction we took secondary acetylenic alcohols of type A, (I)-(IV), and secondary ethylenic alcohols of type B, (V)-(VIII), whose preparation and properties we have described previously [10]. (See top of following page for scheme.)

In the reaction of the acetylenic alcohols (I)-(IV) with acetoacetic ester or ketene dimer the corresponding acetoacetates (XII)-(XV) are formed. The yields of the latter are always higher when ketene dimer is used, but they depend greatly on the reaction conditions, mainly on the catalyst used. The catalysts studied included sodium ethoxide, sodium acetate, pyridine, triethylamine, and aluminum isopropoxide, and for condensation with acetoacetic ester we obtained the best yields (60-65%) in presence of aluminum isopropoxide, while for condensation with ketene dimer we obtained the best yields (70-83%) in presence of triethylamine.

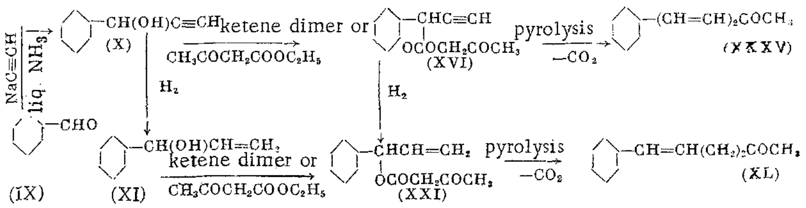
With malonic ester the acetylenic alcohols (I)-(IV) condense with greater difficulty with formation of the (ethoxycarbonyl)acetates (XXIII)-(XXVI) in yields of 36-56%. The selective hydrogenation of the (ethoxycarbonyl)acetates (XXIII)-(XXVI) and the acetoacetates (XVII)-(XX) in presence of Lindlar's catalyst goes



(I), (V), (XII), (XVII), (XXIII), (XXVII), (XXXI), (XXXVI)—$R_1=R_2=R_3=H$
(II), (VI), (XIII), (XVIII), (XXIV), (XXVIII), (XXXII). (XXXVII)—$R_1=CH_3$, $R_2=R_3=H$
(III), (VII), (XIV), (XIX), (XXII), (XXV), (XXIX), (XXXIII), (XXXVIII)—$R_2=CH_3$, $R_1=R_3=H$
(IV), (VIII), (XV), (XX), (XXVI), (XXX), (XXXIV), (XXXIX)—$R_3=CH_3$, $R_1=R_2=H$

readily with formation of the corresponding dienic (ethoxycarbonyl)acetates (XXVII)-(XXX) and acetoacetates (XVII)-(XX). The latter were also obtained by the reaction of the alcohols of type B, (V)-(VIII), with ketene dimer or acetoacetic ester. These alcohols condense more readily with ketene dimer than alcohols of type A do, and the yields of the acetoacetates (XVII)-(XX) attain 80-88%.

The position of the methyl groups in the cyclohexene ring of the original alcohols (I)-(IV) and (V)-(VIII) has a certain effect on their reactivities in the reaction leading to the formation of (ethoxycarbonyl)acetates and acetoacetates. The alcohols (I) and (V), which have no substituents in the ring, and the alcohols (III) and (VII) with a methyl group in the 4-position are somewhat more inert (see below, Tables 1 and 2). The double bond in the ring has no appreciable effect on the yield of acetoacetates. Thus, the cyclohexene alcohols (I) and (V) and the corresponding cyclohexane alcohols (X) and (XI) form acetoacetates in almost identical yields (see below, Table 1).



By the pyrolysis of the acetoacetates (XII)-(XXI) it was expected to obtain the trienic ketones (XXXI)-(XXXIV) the dienic ketones (XXXV)-(XXXIX), and the ethylenic ketone (XL), and from the (ethoxycarbonyl)acetates (XXIII)-(XXX) – the trienic esters (XLII) and the dienic esters (XLIII). Investigation of the pyrolysis of acetoacetates of secondary acetylenic alcohols showed that in all cases* three reactions occur: 1) conversion of the acetoacetates into the desired trienones (XXXI)-(XXXIV); 2) partial hydrolysis of the acetoacetate into the original alcohol and acetoacetic acid with subsequent cleavage of the latter into acetone and carbon dioxide; 3) condensation of the enol and keto forms of the acetoacetate with formation of dehydroacetic acid (XLIV).

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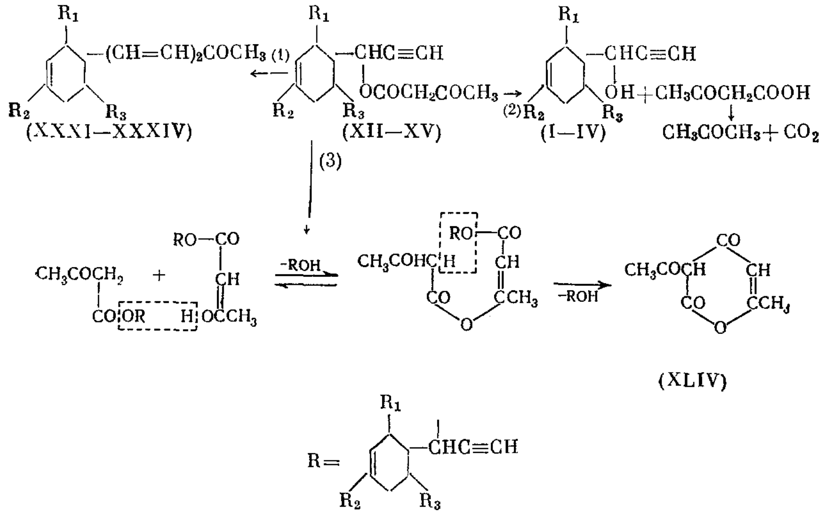
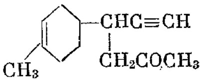
* The pyrolysis conditions (time, temperature, and catalyst) were varied widely.



The yields of the trienones (XXXI)-(XXXIV) depend somewhat on the position of the methyl groups in the cyclohexene ring. Thus, in the case of the acetoacetates (XIII) and (XV) with the substituents R_1 and R_3 the yields of trienones attain 34% (based on the acetoacetate which reacts), as compared with 7-10% in the case of unsubstituted (XII) and the acetoacetate (XIV) with the substituent R_2. With diminution in the yield of the acetoacetate the yield of dehydroacetic acid rises correspondingly from 48 to 65%. It is probable that substituents adjacent to the side chain sterically hinder the condensation of the enol and keto forms with formation of dehydroacetic acid, which explains the higher yields of the trienones (XXXII) and (XXXIV).*

All these considerations apply also to the pyrolysis of the dienic acetoacetates (XVII)-(XX), as a result of which we obtained the dienones (XXXVI)-(XXXIX). The structure of the trienones (XXXI)-(XXXIV) was proved by an investigation of the ultraviolet spectra of their 2,4-dinitrophenylhydrazones (see below, Table 3). The presence of λ_{max} at 390 mμ points to the conjugation of the double bonds and the carbonyl group in the side chain of the trienones (XXXI)-(XXXIV). It should be mentioned that from the pyrolyzate of the acetoacetate (XIV), apart from the trienone (XXXIII), we isolated a ketone whose structure, on the basis of the absence of λ_{max} at 380 mμ in the ultraviolet spectrum of its 2,4-dinitrophenylhydrazone, probably corresponds to the formula (XLI):



(XLI)

The pyrolysis of the (ethoxycarbonyl)acetates (XXIII)-(XXX) under the conditions used for the acetoacetates is accompanied by much resinification and leads mainly to products of the hydrolysis of the original (ethoxycarbonyl)acetates — the original alcohol and malonic ester; only very small amounts of unsaturated esters were formed. Their presence was established by an analysis of the ultraviolet spectra of the pyrolyzates (presence of a maximum at 280 mμ) [11].

EXPERIMENTAL

Condensation of Cyclohexanecarboxaldehyde [12] with Acetylene. At between −60 and −65°C with vigorous stirring acetylene was passed into a solution of 30 g of sodium in 2 liters of liquid ammonia until the blue color of the solution disappeared. Passage of acetylene and stirring was continued at the same temperature while a solution of 140 g of the aldehyde (IX) [b.p. 53-55° (15 mm), n_D^{20} 1.4480] in 250 ml of dimethoxymethane was added dropwise in the course of 30 min. Stirring and passage of acetylene were continued further for 3 h at between −60 and −50°. The cooling bath was then removed and after the evaporation of the most of the ammonia the reaction mixture was decomposed with ammonium chloride. The product was extracted with ether, and the extract was washed with water and dried with

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* It is probable that the absence of steric hindrance explains why only the original alcohol and dehydroacetic acid were obtained in the pyrolysis of the acetoacetate of 3-butyn-2-ol [7].

TABLE 1

No.	Compound	Yield, %		B.p., °C (p, mm)	d_4^{20}	n_D^{20}	MR		Found %		Molecular formula	Calculated %	
		A	B				found	calc.	C	H		C	H
XII	α-Ethynyl-3-cyclohexene-1-methanol acetoacetate	72	60	117-118 (1)	1.0670	1.4890	59.58	59.23	70.79	7.48	$C_{13}H_{16}O_3$	70.89	7.32
XIII	α-Ethynyl-2-methyl-3-cyclohexene-1-methanol acetoacetate	79	62	121-122 (1.5)	1.0566	1.4878	64.33	63.85	71.85	7.86	$C_{14}H_{18}O_3$	71.77	7.74
XIV	α-Ethynyl-4-methyl-3-cyclohexene-1-methanol acetoacetate	58	50	126-127 (2)	1.0570	1.4923	64.42	63.85	71.95	7.67	$C_{14}H_{18}O_3$	71.77	7.74
XV	α-Ethynyl-6-methyl-3-cyclohexene-1-methanol acetoacetate	83	65	125-126 (1.5)	1.0540	1.4892	64.12	63.85	71.64	7.80	$C_{14}H_{18}O_3$	71.77	7.74
XVI	α-Ethynylcyclohexanemethanol acetoacetate	77	-	101-102 (1)	1.0760	1.4770	58.04	57.49	70.29	8.29	$C_{13}H_{18}O_3$	70.27	8.16
XVII	α-Vinyl-3-cyclohexene-1-methanol acetoacetate	77	62	102-103 (1)	1.0413	1.4840	61.05	60.76	70.35	7.95	$C_{13}H_{18}O_3$	70.27	8.16
XVIII	2-Methyl-α-vinyl-3-cyclohexene-1-methanol acetoacetate	87	65	113-114 (2)	1.0297	1.4828	65.58	65.38	71.35	8.52	$C_{14}H_{20}O_3$	71.16	8.53
XIX	4-Methyl-α-vinyl-3-cyclohexene-1-methanol acetoacetate	79	60	110-111 (1.5)	1.0270	1.4845	65.84	65.38	71.28	8.74	$C_{14}H_{20}O_3$	71.16	8.53
XX	6-Methyl-α-vinyl-3-cyclohexene-1-methanol acetoacetate	88	67	106-107 (1)	1.0340	1.4874	65.72	65.38	71.63	8.68	$C_{14}H_{20}O_3$	71.16	8.53
XXI	α-Vinylcyclohexanemethanol acetoacetate	86	-	189-190 (1)	1.0520	1.4710	59.25	59.02	69.75	9.05	$C_{13}H_{20}O_3$	69.61	8.99

TABLE 2

No.	Compound	Yield, %	B.p., °C (p, mm)	d_4^{20}	n_D^{20}	MR		Found %		Molecular formula	Calculated %	
						found	calc.	C	H		C	H
XXIII	α-Ethynyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	41	114–115 (1)	1.0914	1.4780	64.79	65.49	67.00	7.54	$C_{14}H_{18}O_4$	67.18	7.25
XXIV	α-Ethynyl-2-methyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	56	124–125 (1.5)	1.0827	1.4777	69.10	70.10	68.00	7.86	$C_{15}H_{20}O_4$	68.16	7.63
XXV	α-Ethynyl-4-methyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	36	123–124 (1.5)	1.0860	1.4780	68.89	70.10	68.48	7.71	$C_{15}H_{20}O_4$	68.16	7.63
XXVI	α-Ethynyl-6-methyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	56	118–119 (1)	1.0760	1.4760	69.13	70.10	68.10	7.76	$C_{15}H_{20}O_4$	68.16	7.63
XXVII	α-Vinyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	47	110–111 (2)	1.0613	1.4720	66.70	67.02	66.39	7.92	$C_{14}H_{20}O_4$	66.64	7.99
XXVIII	2-Methyl-α-vinyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	58	124–125 (2)	1.0614	1.4720	69.87	71.64	67.90	8.36	$C_{15}H_{22}O_4$	67.64	8.33
XXIX	4-Methyl-α-vinyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	45	119–120 (2)	1.0624	1.4726	69.62	71.64	67.96	8.19	$C_{15}H_{22}O_4$	67.64	8.33
XXX	6-Methyl-α-vinyl-3-cyclohexene-1-methanol (ethoxycarbonyl)acetate	57	115–116 (1.5)	1.0624	1.4750	70.60	71.64	67.78	8.16	$C_{15}H_{22}O_4$	67.64	8.33

TABLE 3

No.	Compound	Yield %	B. p., °C (p, mm)	n_D^{20}	Found %		Molecular formula	Calculated %		2,4-Dinitrophenylhydrazone*						Ultraviolet absorption spectrum†	
					C	H		C	H	M. p., °C	Found %		Molecular formula	Calculated %		λ_{max}, mμ	log ε
											C	H		C	H		
XXXI	6-(3-Cyclohexen-1-yl)-3,5-hexadien-2-one	10	-	-	-	-	$C_{12}H_{16}O$	-	-	207-208	60.38	5.59	$C_{18}H_{20}N_4O_4$	60.66	5.66	225;300; 370;390;	4.3222;4.2355; 4.4031;4.5866
XXXII	6-(2-Methyl-3-cyclohexen-1-yl)-3,5-hexadien-2-one	34	109-110 (1	1.5488	81.55	9.32	$C_{13}H_{18}O$	82.06	9.54	191-192	61.70	5.88	$C_{19}H_{22}N_4O_4$	61.61	5.99	225;275; 300;390	4.3201;4.3493; 4.3945;4.6107
XXXIII	6-(4-Methyl-3-cyclohexen-1-yl)-3,5-hexadien-2-one	7	-	-	-	-	$C_{13}H_{18}O$	-	-	208-210	61.33	5.97	$C_{19}H_{22}N_4O_4$	61.61	5.99	250;275; 355;385	4.2095;4.2625; 4.4814;4.5821
XXXIV	6-(6-Methyl-3-cyclohexen-1-yl)-3,5-hexadien-2-one	32	-	-	-	-	$C_{13}H_{18}O$	-	-	193-194	61.37	6.20	$C_{19}H_{22}N_4O_4$	61.61	5.99	225;275; 300;390	4.3345;4.3181; 4.3655;4.6149
XXXV	6-Cyclohexyl-3,5-hexadien-2-one	36	115-116 (2)	1.5129	80.56	10.14	$C_{12}H_{18}O$	80.85	10.18	203-204	60.68	6.39	$C_{18}H_{22}N_4O_4$	60.32	6.19	270;305; 390	4.2330;4.2672; 4.5441
XLI	4-(4-Methyl-3-cyclohexen-1-yl)-5-hexyn-2-one	3	-	-	-	-	$C_{13}H_{18}O$	-	-	179-180	61.34	5.68	$C_{19}H_{22}N_4O_4$	61.61	5.99	370	-
XXXVII	6-(2-Methyl-3-cyclohexen-1-yl)-5-hexen-2-one	25	-	-	-	-	$C_{13}H_{20}O$	-	-	68-70	61.40	6.68	$C_{19}H_{22}N_4O_4$	61.27	6.48	360	-
XXXVIII	6-(4-Methyl-3-cyclohexen-1-yl)-5-hexen-2-one	18	-	-	-	-	$C_{13}H_{20}O$	-	-	71-72	61.34	6.32	$C_{19}H_{22}N_4O_4$	61.27	6.48	-	-
XXXIX	6-(6-Methyl-3-cyclohexen-1-yl)-5-hexen-2-one	28	117-118 (2)	1.4990	80.87	10.77	$C_{13}H_{20}O$	81.20	10.48	74-75	61.42	6.39	$C_{19}H_{22}N_4O_4$	61.27	6.48	-	-
XL	6-Cyclohexyl-5-hexen-2-one	32	82-84 (0.5)	1.4784	79.52	11.19	$C_{12}H_{20}O$	79.94	11.18	88-89	60.10	6.78	$C_{18}H_{22}N_4O_4$	59.98	6.71	-	-

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* Recrystallized from a 2: 1 mixture of ethyl acetate and methanol.

† The ultraviolet spectra of the 2,4-dinitrophenylhydrazones were determined in ethanol solution.

$MgSO_4$. Vacuum fractionation gave 99 g (63% on the aldehyde that reacted) of α-ethynylcyclohexanemethanol (X); b.p. 67-68° (2 mm); n_D^{20} 1.4798; d_4^{20} 0.9538. Found %: C 78.13; H 10.55. MR 40.97. $C_9H_{14}O$. Calculated %: C 78.14; H 10.21. MR 41.085. The literature [13] gives: b.p. 178-179° (745 mm); n_D^{20} 1.4820; d_4^{20} 0.9870.

Selective Hydrogenation of the Alcohol (X). 21.35 g of the acetylenic alcohol (X) was hydrogenated in absolute methanol in presence of Lindlar's catalyst; 3600 ml of hydrogen was absorbed. Catalyst was filtered off, solvent was driven off, and the hydrogenation product was vacuum-distilled. We obtained 18.5 g (86%) of α-vinylcyclohexanemethanol (XI); b.p. 51-52° (1 mm); n_D^{20} 1.4753. Found %: C 77.40; H 11.66. $C_9H_{16}O$. Calculated %: C 77.10; H 11.49.

Acetoacetates (XII)-(XVI). A) 0.65 mole of ketene dimer was added with stirring at 2-5° in the course of 1 h to a mixture of 0.5 mole of the acetylenic alcohol (I), (II), (III), (VI), or (X) and 0.5 ml of triethylamine. The reaction mixture was stirred for 2 h at room temperature and for 1 h at 60°. The reaction product was washed several times with saturated sodium bicarbonate solution and was extracted with ether; the extract was washed with water until neutral and dried with $MgSO_4$. After the removal of solvent, the residue was vacuum-distilled. The constants and yields of the acetoacetates obtained are given in Table 1.

B) A mixture of 0.165 mole of the acetylenic alcohol (I), (II) (III), (IV), or (X) and 0.33 mole of acetoacetic ester was heated for 24 h at 170-180° without catalyst or with aluminum isopropoxide. Unchanged acetoacetic ester and acetylenic alcohol were vacuum-distilled off. The residue was treated as in the preceding experiment. The constants of the acetoacetates obtained agree with the constants of those prepared by method A. The yields are stated in Table 1.

Acetoacetates (XVII)-(XXI). By the action of 0.3 mole of ketene dimer on 0.25 mole of the ethylenic alcohol (V), (VI), (VII), (VIII), or (XI) under the conditions of method A we obtained the acetoacetates (XVII)-(XXI). Their yields and constants are given in Table 1.

0.165 mole of the acetoacetate (XII), (XIII), (XIV), (XV), or (XVI) was selectively hydrogenated in absolute methanol in presence of Lindlar's catalyst. When hydrogenation stopped, the catalyst was filtered off, and the hydrogenation product was vacuum-distilled. The constants of the acetoacetates obtained agree with those of the corresponding acetoacetates obtained in the preceding experiment (see Table 1).

Exhaustive Hydrogenation of the Acetoacetate (XII). 9.5 g of the acetoacetate (XII) was hydrogenated in 20 ml of absolute methanol in presence of palladium catalyst. 3800 ml of hydrogen was absorbed. Catalyst was filtered off, solvent was removed, and the hydrogenation product was vacuum-distilled. We obtained 6.85 g of α-ethylcyclohexanemethanol acetoacetate (XXII); b.p. 103° (1 mm); n_D^{20} 1.4680; d_4^{20} 1.0542. Found %: C 69.00, 68.75; H 9.80, 10.01. MR 64.12. $C_{14}H_{22}O_3$. Calculated %: C 68.99; H 9.79. MR 63.85.

(Ethoxycarbonyl)acetates (XXIII)-(XXVI). A mixture of 0.165 mole of the acetylenic alcohol (I), (II), (III), or (IV) and 0.33 mole of malonic ester was heated for 36 h at 170-175°. Unchanged reactants were vacuum-distilled off. The residue was washed with saturated sodium bicarbonate solution and extracted with ether; the extract was washed with water and dried with $MgSO_4$. Solvent was removed, and the residue was vacuum-distilled. The constants and yields of the (ethoxycarbonyl)acetates obtained are given in Table 2.

(Ethoxycarbonyl)acetates (XXVII)-(XXX). A mixture of 0.1 mole of the ethylenic alcohol (V), (VI), (VII), or (VIII) and 0.2 mole of malonic ester was heated for 36 h at 170-175°. After treatment analogous to that described for the preceding experiment we obtained the (ethoxycarbonyl)acetates whose constants and yields are given in Table 2.

The (ethoxycarbonyl)acetates (XXIII)-(XXVI) (0.05 mole) were selectively hydrogenated in absolute methanol in presence of Lindlar's catalyst. The constants of the (ethoxycarbonyl)acetates obtained agreed with the constants of those obtained in the preceding experiment (see Table 2).

Pyrolysis of the Acetoacetates (XII)-(XXI). A mixture of 0.1 mole of the acetoacetate (XIII), 0.05 g of p-toluenesulfonic acid, and 0.1 g of hydroquinone was heated in a Claisen flask at 190 to 210° for 45 min. In the course of the pyrolysis 560 ml of carbon dioxide came off and at 55-60°, 0.4 g of acetone distilled over (n_D^{20} 1.3650, 2,4-dinitrophenylhydrazone, m.p. 124-125°, undepressed by admixture with a known sample). The pyrolyzate was vacuum-distilled: Fraction I – 73-78° (1.5 mm); n_D^{20} 1.4980;

8.2 g; Fraction II — 110-115° (1.5 mm); n_D^{20} 1.5112; 2.6 g; Fraction III — 115-120° (1.5 mm); n_D^{20} 1.5055; 1.6 g; Fraction IV — 120-124° (1.5 mm); n_D^{20} 1.4950; 3.0 g. The resinous residue (6.8 g) was dissolved in ethyl acetate and precipitated with petroleum ether. We obtained 4.1 g of an amorphous yellow powder; after a number of crystallizations we obtained dehydroacetic acid, m.p. 107-108°, undepressed by admixture of a known sample. Fraction I was the original acetylenic alcohol (II); Fractions II and III were mixtures of the trienic ketone (XXXII) and unchanged acetoacetate (XIII); and Fraction IV was the acetoacetate (XIII). However, we did not succeed in isolating analytically pure trienones (XXXI)-(XXXIV) and dienones (XXXV) to (XXXIX) either by vacuum distillation or with the aid of the Girard P reagent.

4.2 g of a mixture of Fractions II and III was chromatographed on 350 g of alumina (activity II). By elution with a mixture of petroleum ether and benzene we isolated 1.7 g of the trienone (XXXII) (yield 34%, based on the acetoacetate which took part in the decarboxylation reaction). By elution with a mixture of ether and methanol we isolated 2.1 g of the acetoacetate (XIII).

The pyrolysis of the acetoacetates (XII)-(XXI) was conducted in a similar way. We did not succeed in isolating the unsaturated ketone (XXXVI) in an analytically pure state; the 2,4-dinitrophenylhydrazone of this ketone is not a crystalline substance.

The constants and yields of the unsaturated ketones and their crystalline derivatives are given in Table 3.

CONCLUSIONS

Acetoacetic and (ethoxycarbonyl)acetic esters of α-ethynyl- and α-vinyl-3-cyclohexene-1-methanols were synthesized, and their pyrolysis was studied.

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