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DUAL REACTIVITY OF SODIUM ETHYL ACETOACETATE AND ACETYLACETONATE BY ALKYLATION WITH ALKYL HALIDES

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It was believed till the recent years that by alkylating sodium ethyl acetoacetate and sodium acetylacetonate with alkyl halides exclusively the C-alkylating takes place and only ethyl α-alkylacetoacetates and 3-alkylacetylacetonates are formed: $CH_3COCHRCOOC_2H_5$ and $CH_3COCHRCOCH_3$.

In 1963 American authors (1) alkylating the ethyl acetoacetate with sec- butyl iodide under ordinary alkylating conditions (ethanolic sodium ethoxide) revealed besides the main product of reaction (ethyl α-sec-butylacetoacetate) the presence of an isomeric product-ethyl-β-(sec-butoxy)crotonate $CH_3C(OC_4H_9\text{-}\underline{sec})=CHCOOC_2H_5$. The amount of the latter, as judged by g.l.p.c. was 6 to 8%.

The structure of this product was confirmed by the independent synthesis and by UV,IR and NMR spectrum data.

During the recent years we investigated (2,3,4) the solvent effect on keto-enol equilibrium in ethyl α-alkylacetoacetates and 3-alkylacetylacetones, received by alkylating.

The work of the American authors (1) made us reinvestigate these reactions, to determine whether O-alkylation is a regular component and whether it depends on the alkyl halide structure.

Alkylating of sodium ethyl acetoacetate (received from ethyl acetoacetate and ethanolic sodium ethoxide) was performed by boiling with alkyl bromides. Dry sodium acetylacetone was heated for some hours at 140-160° with alkyl iodides in sealed tubes in an autoclave.

The resolving of all received mixtures after distilating was carried out by g.l.p.c. on Willy Giede (DDR) Model GCHF-18 chromatograph with a catharometer. The 2 m.long, 6 mm stainless steel column was packed with the boiled butter (5) on diatomaceous brick (20% $^{w}/w$). The column temperature was 120-160°,with helium carrier gas flow rate at approximately 60 ml.per.min.

In most cases the presence of O-alkylated products was revealed.

The quantitative estimation of O-derivatives was carried out when their amount in reaction mixture was not less then 0,5%.

The amounts in percents are listed in table 1.

The increasing of O-alkylated products by passing from alkyl halides with normal radicals to those with branched radicals is to be noticed. That may be explained by growing of steric hindrances at the formation of C-alkylated products (6,7). Most clearly it is seen in the case of acetylacetone. Here the formation of O-ethers by alkylating with iso-propyl iodide and sec-butyl iodide becomes a concurrent reaction.

TABLE 1

Amounts of O-alkylated products in the mixture after alkylating sodium ethyl acetoacetate and sodium acetylacetone in percents.

R	O-ether percentage	
	$CH_3C(OR)=CHCOOC_2H_5$	$CH_3C(OR)=CHCOCH_3$
CH_3	about 1	0
C_2H_5	3	0
n-C_3H_7	4	3
n-C_4H_9	5	5
iso-C_3H_7	9	27
iso-C_4H_9	5	3
sec-C_4H_9	8	35
cyclopentyl	5	-

For identification of O-alkylated products ethyl ß-alkoxycrotonates were received from ethyl ß-chlorocrotonate $CH_3CCl=CHCOOC_2H_5$ and 2-alkoxy-2-penten-4-ons $CH_3C(OR)=CHCOCH_3$ from 2-chlor-2-penten-4-on by means of exchange reactions with sodium alkoxides. The properties of received O-ethers are listed in table 2.+)

As far as all the ethyl α-alkylacetoacetates and 3-alkylacetylacetones described above by us and other authors were contaminated by O-alkylated products, we were to receive pure C-alkylated products from reaction mixtures.

The C- and O-alkylated products could not be separated by fraction distillation. The contaminating O-derivatives were removed from C-alkylated products by shaking with 2N HCl for 12-40 hours at room temperature. The purity of C-alkylated products was controled by g.l.p.c.

In tables 3 and 4 the properties of pure compounds are listed.

Ethyl α-isopropylacetoacetate was received by alkylating ethyl acetoacetate with isopropanol in the presence of BF_3 (10) and, naturaly,was not contaminated by the O-alkylated product.

The results of investigation of the solvent effect on keto-enol equilibrium of C-alkylated derivatives are in progress.

+) probably <u>trans-</u>

TABLE 2

Properties of ethyl ß-alkoxycrotonates and 2-alkoxy-2-penten-4-ons

R	b.p./mm	n_D^{20}	d_4^{20}	Found %C	Found %H	Calc. %C	Calc. %H
$CH_3C/OR/=CHCOOC_2H_5$							
C_2H_5 *)	m.p.30-31°	-	-	-	-	-	-
iso-C_3H_7	64-65/4	1.4515	0.9532	62.4 62.3	8.9 8.9	62.8	9.3
sec-C_4H_9	98-100/9	1.4535	0.9552	64.6 64.6	9.8 9.8	64.5	9.8
Cyclopentyl	126-128/8	1.4800	1.0184	66.8 66.6	9.2 9.3	66.6	9.2
*) Lit.data(8) m.p.30.2°							
$CH_3C/OR/=CHCOCH_3$							
C_2H_5 **)	83-85/22	1.4600	0.9468	65.1 65.4	9.3 9.5	65.6	9.4
iso-C_3H_7	64-65/4	1.4615	0.9281	62.4 62.3	8.9 8.9	62.8	9.3
sec-C_4H_9	58-60/5	1.4648 /by 21.5°/	0.9155	68.8 69.1	10.4 10.7	69.2	10.3
**) Lit.data (9) b.p.71-72°/15mm, n_D^{25} 1.4612, d_4^{20} 0.94							

TABLE 3

Properties of ethyl α-alkylacetoacetates

$CH_3COCHRCOOC_2H_5$

R	b.p./mm	n^{20}_D	d^{20}_4	Contamin. by O-isomer in percents	Found		Calc.	
					% C	% H	% C	% H
CH_3	61-62/6	1.4205	1.0027	0	58.2 58.0	8.3 8.3	58.3	8.3
C_2H_5	70-71/7	1.4240	0.9791	0.5	60.9 60.9	8.9 8.8	60.7	8.9
n-C_3H_7	106-107/22	1.4255	0.9653	traces	62.4 62.5	9.3 9.3	62.8	9.4
n-C_4H_9	97-99/5	1.4302	0.9560	1	64.8 64.9	9.8 9.9	64.5	9.8
<u>iso</u>-C_3H_7	96-97/20	1.4252	0.9596	0	62.9 63.0	9.6 9.6	62.8	9.4
<u>sec</u>-C_4H_9	108-109/20	1.4315	0.9591	0	64.8 64.8	9.9 10.1	64.5	9.8
Cyclopentyl	118-120/11	1.4532	1.0109	0.5	67.0 67.1	9.0 9.2	66.6	9.2

TABLE 4

Properties of 3-alkylacetylacetones

$CH_3COCHRCOCH_3$

R	b.p./mm	n_D^{20}	d_4^{20}	Contamin. by O-isomer in percents	Found		Calc.	
					% C	% H	% C	% H
CH_3	46.5-48.5/8	1.4420	0.9760	0	62.5 62.8	8.8 8.8	63.1	8.9
C_2H_5	76/20	1.4419	0.9568	0	65.2 65.1	9.3 9.3	65.6	9.4
n-C_3H_7	86-88/16	1.4445	0.9409	< 0.5	67.8 67.8	10.0 9.9	67.6	9.9
n-C_4H_9	96-97/14	1.4470	0.9267	traces	69.4 69.1	10.4 10.5	69.2	10.3
iso-C_4H_9	94-96/18	1.4461	0.9283	< 1	69.3 69.2	10.2 10.4	69.2	10.3
iso-C_3H_7	70-71/12	1.4325	0.9234	0	67.2 67.3	9.9 9.9	67.6	9.9
sec-C_4H_9	78-80/10	1.4402	0.9343	< 0.5	69.0 69.0	10.2 10.3	62.2	10.3

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