

Calculated: C 74.11; H 12.22; N 3.09%; NE 453.8.

N-Butylamide of Decylsuccinic Acid (IV) and Its Hydrolysis. The homolytic alkylation of succinimide with 1-decene [6] gave decylsuccinimide (V) in 58% yield, mp 91-92°. Found: C 69.93; H 10.41; N 5.88%.  $C_{14}H_{25}O_2N$ . Calculated: C 70.29; H 10.46; N 5.86%. A mixture of 10 g of (V), 10.5 g of n-butyl bromide, 6.3 g of  $K_2CO_3$ , and 50 ml of DMF was stirred for 1 h at  $\sim 20^\circ$ , and then it was heated on the steam bath for 18 h until the  $CO_2$  evolution ceased, mixed with cracked ice, and extracted with benzene. The benzene was evaporated, while the residue (IV) was dissolved in 30 ml of ethanol, mixed with 5 ml of 40% NaOH solution and heated on the steam bath for 3 h. Then the mixture was cooled, neutralized with dilute HCl solution, and extracted with benzene. The extract was washed with water, dried, and evaporated. The residue was recrystallized from heptane to give 9.5 g (72%) of (IV), mp 58-59°. Found: C 69.02; H 11.37; N 4.45%; NE 315.8.  $C_{18}H_{35}O_3N$ . Calculated: C 68.96; H 11.26; N 4.47%; NE 313.5.

#### CONCLUSIONS

1. Alkylsuccinic anhydrides react with monoalkylamines in two directions to give approximately equimolar amounts of the N-alkylamides of 2-carboxymethyl- and 3-carboxyalkanoic acids.

2. The hydrolysis of an alkylsuccinic acid N-alkylimide with aqueous NaOH solution is regioselective and leads to the formation of the 2-carboxymethylalkanoic acid N-alkylamide.

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#### FREE RADICAL ADDITION OF ALKANOIC ESTERS TO ALKYL MALEATES

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As a continuation of studying the free radical addition of ethers and esters of alkyl maleates (AM) [1, 2], we studied in the present paper the behavior of the esters  $CH_3(CH_2)_nCOOR$  (Ia-e) (see Scheme), and also of butyl isobutyrate (II), hexyl acetate (III), octyl formate (IV), butyrolactone (V), and ethyl benzoate (VI) in this reaction. The purpose of this study was to evaluate the ability of the mentioned esters to form the homolytic addition products to AM and ascertain the specific traits of the homolytic reactions that lead to these products.

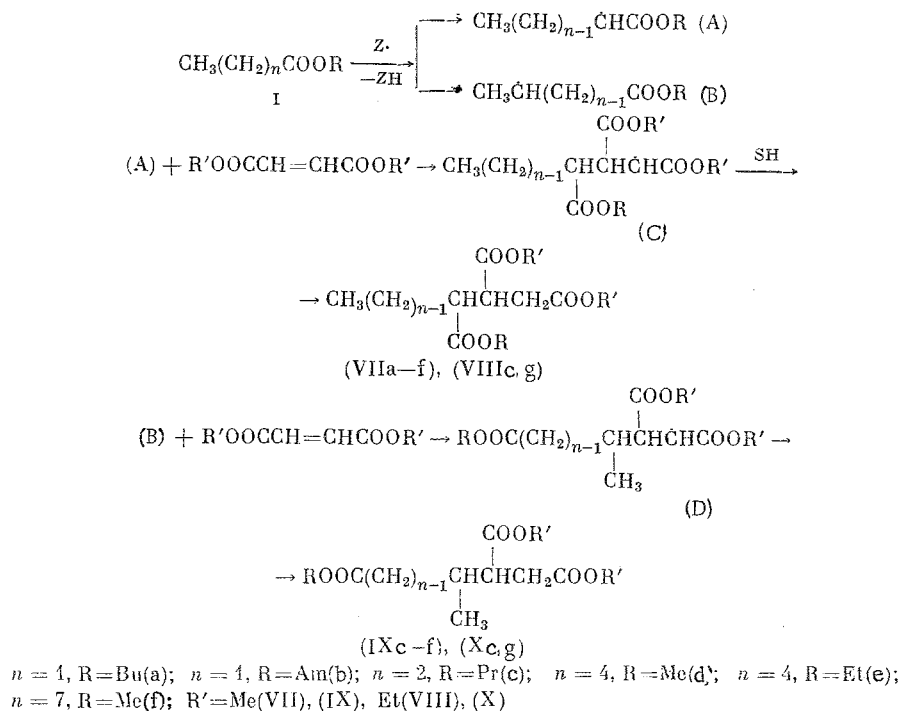
The reactions were run at 140-180°C and the ester:AM ratio was 10:1. As the initiator we used tert-butyl peroxide (20 mole % of the AM). Under these conditions the AM reacted to the extent of 82-92% with the studied esters. Butyl isobutyrate was an exception, and here the AM conversion was only half as great (Table 1). The main components of the isolated fractions proved to be the (VII) adducts in the case of the addition products of the butyl (Ia) and amyl (Ib) propionates to methyl maleate (MM), the (VIII) adducts when addition is to ethyl maleate (EM), the (VII) and (IX) adducts in the case of the addition products of esters (Ic-d) (see Scheme) to MM, and adducts (VIII) and (X) when addition is to EM, which

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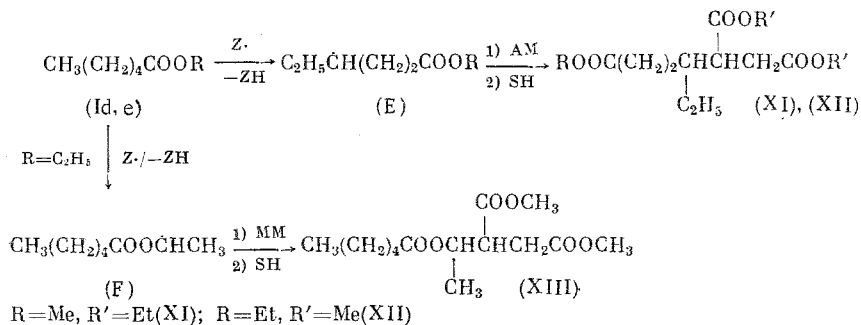
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 8, pp. 1842-1853, August, 1980. Original article submitted August 16, 1979.

indicates that radicals (1) and (2) ( $Z\cdot$  are the radicals that are formed in the system, and SH is the donor of H atoms) take part in the reaction:

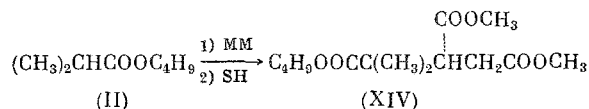
Scheme



Besides compounds (VII)-(X), the fractions of the 1:1 adducts, obtained from the methyl (Id) and ethyl (Ie) hexanoates, contained a small amount (14 rel. %) of adducts (XI) and (XII), the AM addition products at the ( $\omega$ -2)-C atom of these esters, and also a substantial amount of adduct (XIII) in the case of ester (Ie), which indicates the formation of four types of radicals from this ester under the reaction conditions, and specifically (A), (B), (E), and (F)



From butyl isobutyrate (II) and MM, just as from the propionates, only one adduct - dimethyl 3-methyl-3-butoxycarbonylbutane-1,2-dicarboxylate (XIV) - was obtained



As a result, in the case of the methyl, propyl, butyl, and amyl esters of alkanolic acids with 3-9 C atoms the AM adds only to the acyl group of the ester, and here it adds regioselectively in the case of the propionates and isobutyrate, at the  $\alpha$ -C atom of their acyl group, at the  $\alpha$ - and ( $\omega$ -1)-C atoms in an  $\sim$ 1:1 ratio in the case of the butyrate, and at the  $\alpha$ -, ( $\omega$ -1)-, and ( $\omega$ -2)-C atoms in the case of the hexanoates and nonanoates. It is important to mention that in the homolytic addition of alkanolic esters to 1-alkenes under analogous conditions only the addition products at the  $\alpha$ -C atom of the acyl group of the ester are formed [3].

TABLE 1. Reaction of Esters  $\text{CH}_3(\text{CH}_2)_n\text{COOR}$  with  $\text{R}'\text{OOCCH}=\text{CHCOOR}'(\text{AM})$  (initiator = tert-butyl peroxide)<sup>a</sup>

Expt. No.	Ester	AM (R')	T., °C	Conversion of AM, %	1:1 adducts and their yield, % (based on converted AM)	Residues						Empirical formula of 1:2 adduct			
						yield		mol. wt.		intensity ratio of proton signals of CH <sub>2</sub> O and CH <sub>3</sub> O					
						mole % <sup>b</sup>	weight % <sup>c</sup>	found		calculated <sup>b</sup>	found		calculated <sup>b</sup>	found/calc., %	
														C	H
1	(Ia)	CH <sub>3</sub>	146	85	(VIIa), 27	62	178	438	418	0,18	0,17	$\frac{55,36}{54,54}$	$\frac{7,48}{7,19}$	C <sub>19</sub> H <sub>30</sub> O <sub>10</sub>	
2	(Ib)	CH <sub>3</sub>	164	91	(VIIb), 24	60	188	468	432	0,19	0,17	$\frac{56,44}{55,55}$	$\frac{7,58}{7,40}$	C <sub>20</sub> H <sub>32</sub> O <sub>10</sub>	
3	(Ic)	CH <sub>3</sub>	143	85	(VIIc), 13 (IXc), 13	61	176	425	418	0,18	0,17	$\frac{55,17}{54,54}$	$\frac{7,21}{7,19}$	C <sub>19</sub> H <sub>30</sub> O <sub>10</sub>	
4	(Ic)	C <sub>2</sub> H <sub>5</sub>	143	82	(VIIc), 14 (Xc), 12	59	179	505	474						
5	(Id)	C <sub>2</sub> H <sub>5</sub>	147	86	(VIIId), 11 (Xd), 11	65	209	489	474	2,72	2,66	$\frac{58,67}{58,23}$	$\frac{8,03}{8,02}$	C <sub>23</sub> H <sub>38</sub> O <sub>10</sub>	
6	(Id) <sup>b</sup>	C <sub>2</sub> H <sub>5</sub>	147	82	(XI), 3,5 (VIIId), 18 (Xd), 18	58	104	472	474	2,70	2,66				
7	(Ie)	CH <sub>3</sub>	166	95	(XI), 4,5 (VIIe), 12 (IXe), 12	44	81	459	432	d	d	$\frac{56,08}{55,55}$	$\frac{7,51}{7,40}$	C <sub>20</sub> H <sub>32</sub> O <sub>10</sub>	
8	(If)	CH <sub>3</sub>	180	93	(XII), 4,5 (XIII), 15 (VIIIf), 12	62	169	514	460						
9	(II)	CH <sub>3</sub>	142	48	(IXf), 8 <sup>e</sup> (XIV), 21	59	210	446	432	0,18	0,17	$\frac{56,25}{55,55}$	$\frac{7,59}{7,40}$	C <sub>20</sub> H <sub>32</sub> O <sub>10</sub>	

<sup>a</sup> Taken 0.7 mole of ester (1.4 moles in Expt. 6), 0.07 mole of AM, and 0.014 mole of initiator. The AM was added to the reaction in 4 h, and then the reaction mixture was heated for another 2 h.

<sup>b</sup> On the assumption that the residue consists mainly of the 1:2 adducts.

<sup>c</sup> Of the total weight of the 1:1 adducts.

dPMR spectrum of residue ( $\delta$ , ppm, relative intensity, %): 0.9 t (9), 1.2-1.6 m (28), 2.4 m (10), 2.9 m (10), 3.6 s (37), 4.1 m (5), 5.1 m (~0.5).

<sup>e</sup> Besides (VIIIf) and (IXf), the reaction product contained unidentified substances, probably their isomeric 1:1 adducts, in a total yield of ~8%.

TABLE 2. H-Donor Capacity ( $k_1/k_2 \cdot \Sigma H$ ) of Esters  $\text{CH}_3(\text{CH}_2)_n\text{COOCH}_3$  toward tert-Butoxy Radicals as a Function of n (135°)\*

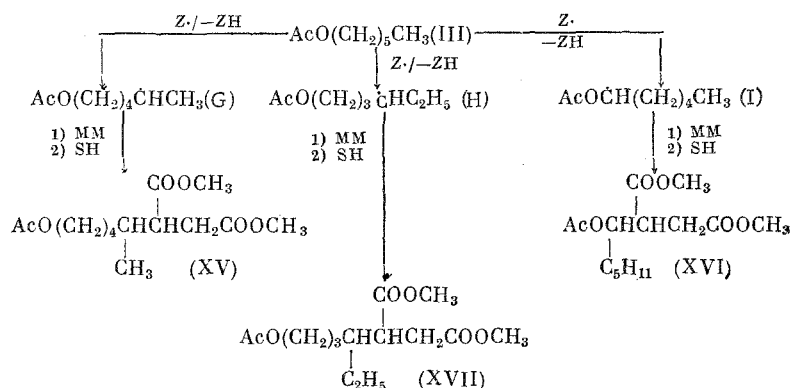
H-donor capacity	Value of n (ester)						
	1	2	3	butyl propionate	4	5	8
Number of H atoms in ester	8	10	12	14	14	16	22
tert-butanol:acetone	0,54	1,19	1,85	2,14	2,66	3,51	5,11
$k_1/k_2$	0,05	0,14	0,27	0,29	0,42	0,59	1,10
$\frac{k_1}{k_2 \cdot \Sigma H} \cdot 10^3$	0,62	1,40	2,25	2,07	3,00	3,68	5,00
$\frac{k_1}{k_2 \cdot \Sigma(\text{CH}_2)} \cdot 10^2$	2,5	3,5	4,5	3,6	5,2	5,9	6,9

\*This capacity was estimated by the method based on the competing reactions (1) and (2) ( $\text{RH} = \text{ester}$ ):  $(\text{CH}_3)_3\text{CO}^\cdot + \text{RH} \xrightarrow{k_1} (\text{CH}_3)_3\text{COH} + \text{R}^\cdot$  (1)  
 $(\text{CH}_3)_3\text{CO}^\cdot \xrightarrow{k_2} \text{CH}_3\text{COCH}_3 + \dot{\text{C}}\text{H}_3$  (2) and the relative amounts of tert-butanol and acetone, formed during the thermal decomposition of the tert-butyl peroxide in the substrate, were determined as described in [5].

The nonselective addition of esters (Ic-f) to the AM is apparently due mainly to the nonselective cleavage of H atoms from these esters by the growing radicals and, when compared with 1-alkenes, the higher ability of maleic acid and its derivatives to add free radicals [4], which does not permit the isomeric radicals, formed from the esters during chain transfer, and in particular (B), (E), and (F), to isomerize completely to the more stable (A) radicals. The absence of selectivity during chain transfer in the homolytic reactions of alkanolic esters with AM is related to the fact that the growing radicals in this case have an electrophilic character. Due to the polar effect, this property of theirs facilitates the cleavage by them of H atoms from the nucleophilic portion of the addend and hinders their analogous reaction with the less stable in the addend, but more electrophilic C-H bonds in the  $\alpha$ -position to the COOR group. A clearer concept of the effect of the polar factor on the ability of electrophilic radicals to cleave H atoms from esters is furnished by the relation given in Table 2 that describes the H-donor capacity of the (I) addends toward tert-butoxyl radicals as a function of the structure of (I).

From the data given in Table 2, it is clear that the H-donor capacity of the C-H bonds in the (I) esters, expressed as the ratio  $k_1/k_2 \cdot \Sigma H$ , increases noticeably with increase in their distance from the alkoxycarbonyl group of the ester. This conclusion follows even more clearly from a comparison of the results obtained for the isomeric methyl hexanoate ( $n = 4$ ) and butyl propionate. In its H-donor capacity the latter is even inferior to methyl pentanoate, which has one  $\text{CH}_2$  group less.

In the case of hexyl acetate (III) the AM adds only to the alkoxy group, and here the addition products at the  $\alpha$ -, ( $\omega$ -1)-, and ( $\omega$ -2)-C atoms of this group are obtained, and specifically adducts (XV), (XVI), and (XVII) in respective yields of 13, 4, and 3% (Table 3)



The probable closeness in the addition rates of radicals G and H to the AM and the chain transfer rates of the formed adduct-radicals to the ester makes it possible to assume that the ratio of adducts (XV) and (XVII) corresponds to the ratio of their steady-state concentrations in the system.

TABLE 3. Reaction of Hexyl Acetate (III), Octyl Formate (IV), Butyrolactone (V), and Ethyl Benzoate (VI) with Methyl Maleate (MM) (180°, initiator = tert-butyl peroxide)<sup>a</sup>

Expt. No.	Ester	Conversion of MM, %	Reaction products and their yield, in % when based on converted MM	Residue						Empirical formula of 1:2 adduct
				yield		mol. wt.		found/calculated, %		
				mole % <sup>b</sup>	weight % <sup>c</sup>	found	calc.	C	H	
1	(III)	92	(XV), 13; (XVI), 4; (XVII), 3	65	237	475	432	56,07 55,55	7,47 7,41	C <sub>20</sub> H <sub>32</sub> O <sub>10</sub> <sup>d</sup>
2	(VI)	100	(XVIII), 12; (XIX), 5; (XX), 12; octane (1.62 d)	—	205	511				
3	(V)	88	(XXI), 50; (XXII), 12		33					
4	(VI)	87	(XXIII), 13	71	418	444	438	57,26 57,53	6,06 5,94	C <sub>21</sub> H <sub>28</sub> O <sub>10</sub> <sup>e</sup>
5	(VI)	85	(XXIII), 41	49	88	441	438	57,42 57,53	6,01 5,94	C <sub>21</sub> H <sub>26</sub> O <sub>10</sub>
6	(VI)	93	(XXIII), 8	83	742	452	438	57,18 57,53	6,03 5,94	C <sub>21</sub> H <sub>28</sub> O <sub>10</sub>

<sup>a</sup>Taken: 0.7 mole of ester (2.1 moles in Expt. 5), 0.07 mole of MM, and 0.014 mole of initiator. The MM was added to the reaction in 3 h, and then the reaction mixture was heated for another 2 h; in Expt. 6 the MM was added to the ester (VI) before the start of reaction.

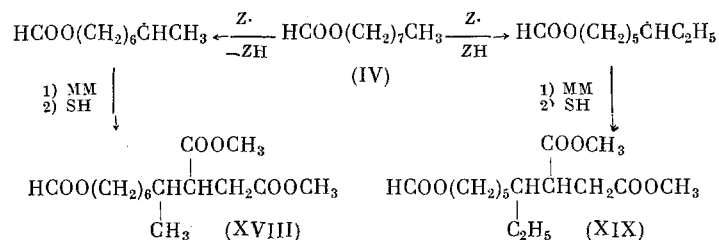
<sup>b</sup>On the assumption that the residue consists mainly of the 1:2 adducts.

<sup>c</sup>Of the total weight of the 1:1 adducts.

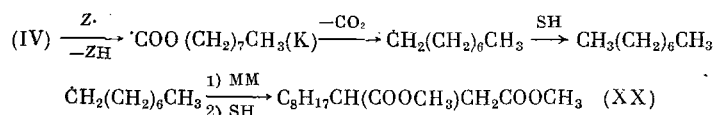
<sup>d</sup>Intensity ratio of proton signals of CH<sub>3</sub>COO and CH<sub>3</sub>O groups: found 0.31; calculated for 1:2 adduct 0.33.

<sup>e</sup>PMR spectrum (δ, ppm): 1.2 d (3H, CH<sub>3</sub>), 2.6 m (2H, CH<sub>2</sub>COO), 3.1 m (3H, CHCOO), 3.6 s (12H, CH<sub>3</sub>O), 5.1 m (1H, CH-O), 7.5 and 8.0 m (5H, C<sub>6</sub>H<sub>5</sub>).

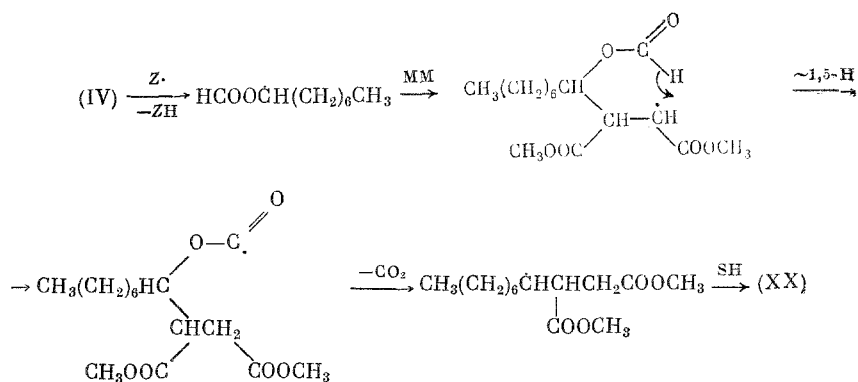
Octyl formate (IV), like hexyl acetate, forms with the AM only the adducts to the alkoxy group of the ester, but, in contrast to the latter, the addition product at its α-C atom was not detected here:



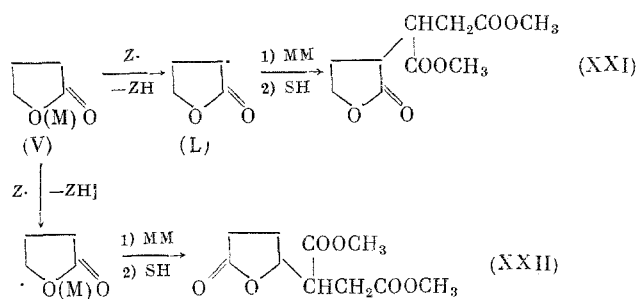
Besides (XVIII) and (XIX), the obtained reaction mixture contained a substantial amount of dimethyl octylsuccinate (XX) and octane (see Table 3). This result, and also the data given in [6, 7], indicate the efficient fragmentation of the alkoxy carbonyl radicals (K) with the elimination of CO<sub>2</sub>, and the subsequent addition of the formed octyl radical to the AM and its cleavage of an H atom from the medium.



The absence of the adduct at the α-CH<sub>2</sub> group of octyl formate in the reaction product of (IV) with MM is probably related to a similar fragmentation, depicted in the scheme given below.

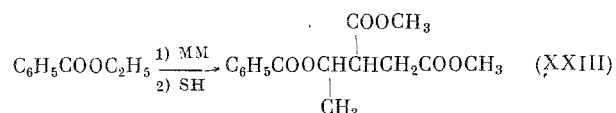


Of the studied esters,  $\gamma$ -butyrolactone (V) proved to be the most capable of forming adducts with the AM. It adds to MM at the  $\alpha$ - and  $\gamma$ -C atoms to give the  $\alpha$ - and  $\gamma$ -(1,2-dicarbomethoxyethyl)-substituted butyrolactones (XXI) and (XXII) in an overall yield of 62% and an  $\sim 4:1$  ratio.



This ratio of (XXI) and (XXII) does not change when all of the MM is added to the reactor before the start of reaction, which testifies to the absence of intermolecular isomerization of radicals (M) and (L), and also to the existence of a higher steady-state concentration of the latter to the existence of a higher steady-state concentration of the latter in the system when compared with the (M) radicals.

Ethyl benzoate (VI) adds regioselectively to MM to give dimethyl  $\alpha$ -benzoyloxyethylsuccinate (XXIII) (13% yield).



The yield of (XXIII) increases to 41% if a 30-fold mole excess of (VI) is used, and drops to 8% if all of the MM is added to the reaction before the start of experiment (Table 3). The composition and structure of the 1:1 adducts were established on the basis of the elemental analysis data, and also the PMR and mass spectral data (Tables 4 and 5).

After isolating the 1:1 adducts from the reaction products the residues represented viscous undistillable oils. The data obtained when determining the molecular weights of the latter and the intensity ratios of the methyl protons of the  $\text{C}_2\text{H}_5\text{O}$  and  $\text{CH}_3\text{O}$  groups in their PMR spectra make it possible to assume that the main components of these oils are the 2:1 adducts of the alkyl maleates with esters (Ia-f) and (II)-(VI).

#### EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD chromatograph, equipped with a flame-ionization detector, in a nitrogen stream (30 ml/min). The columns were: a) 2 m  $\times$  3 mm, packed with 10% DS-550 deposited on Chromosorb W (0.2-0.25 mm); b) 2 m  $\times$  3 mm, packed with 15% PEGS deposited on Chromosorb W (0.2-0.25 mm); c) 1 m  $\times$  3 mm, packed with 5% SE-30 deposited on Chromaton N (0.16-0.2 mm). The mass spectra of the reaction products were obtained on a Varian MAT CH-111 instrument, using chromatographic insertion and an energy of 50 eV for the ionizing ions. The mass spectra of the pure compounds were obtained on a Varian MAT CH-6 instrument, using the system of direct insertion of the substance into the ion source at 70 eV. The PMR spectra were taken on a BS-497 instrument (100 MHz), using either TMS or  $\text{CHCl}_3$ .

TABLE 4. Properties of Adducts (VII)-(XXIII)\*

Adduct	bp, °C (p, mm Hg)	$n_D^{25}$	Found/calculated, %		Empirical formula	PMR spectrum ( $\delta$ , ppm)
			C	H		
(VIIa)	112-116 (0.3)	1.4438	$\frac{56.78}{56.93}$	$\frac{7.99}{8.03}$	$C_{13}H_{22}O_6$	0.9 t (3H, CH <sub>3</sub> ), 1.41 d and 1.43 d (3H, CH <sub>3</sub> ), 1.3 and 1.5 m (4H, CH <sub>2</sub> ), 2.5 m (2H, CH <sub>2</sub> COO), 3.0 m (2H, CHCOO), 3.61 and 3.63 s (6H, CH <sub>3</sub> O), 4.0 t (2H, CH <sub>2</sub> O)
(VIIb)	128-132 (0.4)	1.4462	$\frac{58.06}{58.33}$	$\frac{8.19}{8.33}$	$C_{14}H_{24}O_6$	0.9 t (3H, CH <sub>3</sub> ), 1.40 and 1.42 d (3H, CH <sub>3</sub> ), 1.3 and 1.5 m (6H, CH <sub>2</sub> ), 2.5 m (2H, CH <sub>2</sub> COO), 3.0 m (2H, CHCOO), 3.6 and 3.62 s (6H, CH <sub>3</sub> O), 4.0 t (2H, CH <sub>2</sub> O)
(VIIc)+(IXc) (~1:1)	110-122 (0.25)		$\frac{56.58}{56.93}$	$\frac{7.89}{8.03}$	$C_{13}H_{22}O_6$	0.9 t and d (6H, CH <sub>3</sub> ), 1.6 m (3H, CH <sub>2</sub> ), 2.1 m (~0.5, CH), 2.3 and 2.6 m (~3H, CH <sub>2</sub> COO), 3.0 m (~1.5H, CHCOO), 3.62 and 3.64 s (6H, CH <sub>3</sub> O), 4.1 t (2H, CH <sub>2</sub> O)
(VIIfc)+(Xc) (~1:1)	130-138 (0.2)		$\frac{59.42}{59.60}$	$\frac{8.49}{8.62}$	$C_{13}H_{22}O_6$	
(VIId)	115-118 (0.2)	1.4424	$\frac{59.31}{59.60}$	$\frac{8.46}{8.62}$	$C_{14}H_{24}O_6$	0.9 t (3H, CH <sub>3</sub> ), 1.2 t (6H, CH <sub>3</sub> ), 1.3 and 1.5 m (6H, CH <sub>2</sub> ), 2.6 m (2H, CH <sub>2</sub> COO), 3.0 m (2H, CHCOO), 3.6s (3H, CH <sub>3</sub> O), 4.07 q and 4.09 q (4H, CH <sub>2</sub> O)
(Xd)	126-129 (0.2)	1.4491	$\frac{59.36}{59.60}$	$\frac{8.58}{8.62}$	$C_{13}H_{22}O_6$	0.85 and 0.89 d (3H, CH <sub>3</sub> ), 1.2 t (6H, CH <sub>3</sub> ), 1.3 and 1.5 m (5H, CH <sub>2</sub> and CH), 2.3 t (2H, CH <sub>2</sub> COO), 2.6 m (2H, CH <sub>2</sub> COO), 3.0 m (4H, CHCOO), 3.6 s (3H, CH <sub>3</sub> O), 4.05 q and 4.07 q (4H, CH <sub>2</sub> O)
(VIIe)+(IXe)+(XII)+(XIII) (2:3:1:3)	115-130 (0.3)		$\frac{58.27}{58.33}$	$\frac{8.45}{8.33}$	$C_{14}H_{24}O_6$	0.9 t (12%), 1.2 t, 1.3 and 1.6 m (37%), 2.4 m (13%), 2.9 m (6%), 3.6 s (25%), 4.1 m (6%), 5.1 m (1%)
(VIIf)	142-144 (0.3)	1.4495	$\frac{60.59}{60.76}$	$\frac{8.65}{8.66}$	$C_{16}H_{28}O_6$	0.9 t (3H, CH <sub>3</sub> ), 1.3 and 1.5 m (12H, CH <sub>2</sub> ), 2.6 m (2H, CH <sub>2</sub> COO), 2.9 m (2H, CHCOO), 3.61 and 3.63 s (9H, CH <sub>3</sub> O)
(IXf)	152-155 (0.16)	1.4541	$\frac{60.66}{60.76}$	$\frac{8.59}{8.66}$	$C_{16}H_{28}O_6$	0.86 and 0.90 d (3H, CH <sub>3</sub> ), 1.3 and 1.5 m (14H, CH <sub>2</sub> and CH), 2.3 t (2H, CH <sub>2</sub> COO), 2.6 m (2H, CH <sub>2</sub> COO), 2.9 m (4H, CHCOO), 3.61 and 3.63 s (9H, CH <sub>3</sub> O)
(XIV)	102-106 (0.2)	1.4437	$\frac{58.45}{58.33}$	$\frac{8.57}{8.33}$	$C_{14}H_{24}O_6$	0.9 t (3H, CH <sub>3</sub> ), 1.2s (6H, CH <sub>3</sub> ), 1.4 and 1.6 m (4H, CH <sub>2</sub> ), 2.5 m (2H, CH <sub>2</sub> COO), 2.9 m (4H, CHCOO), 3.62 and 3.63 s (6H, CH <sub>3</sub> O), 4.0 t (2H, CH <sub>2</sub> O)
(XV)	130-133 (0.4)	1.4521	$\frac{58.31}{58.33}$	$\frac{8.21}{8.33}$	$C_{14}H_{24}O_6$	0.86 and 0.89 d (3H, CH <sub>3</sub> ), 1.3 and 1.5 m (7H, CH <sub>2</sub> and CH), 2.0s (3H, CH <sub>3</sub> COO), 2.5 m (2H, CH <sub>2</sub> COO), 2.9 m (4H, CHCOO), 3.61 and 3.63 s (6H, CH <sub>3</sub> O), 4.0 t (2H, CH <sub>2</sub> O)

TABLE 4 (conclusion)

Adduct	bp, °C (p, mm Hg)	$n_D^{22}$	Found/calculated, %		Empirical formula	PMR spectrum ( $\delta$ , ppm)
			C	H		
(XV) + (XVI) + (XVII) (~3:1:1)	124-133 (0.4)	1,4623	58,35 58,33	8,14 8,33	C <sub>14</sub> H <sub>24</sub> O <sub>6</sub>	The spectrum contains a signal with $\delta$ 5,0 ppm (~1%, CH-O) 0,85 and 0,88 d (3H, CH <sub>3</sub> ), 1,3 and 1,5 m (1H, CH <sub>2</sub> and CH), 2,5 m (2H, CH <sub>2</sub> COO), 2,9 m (1H, CHCOO), 3,61 and 3,63 s (6H, CH <sub>3</sub> O), 4,0 t (2H, CH <sub>2</sub> O), 8,0s (1H, CHO)
(XVIII)	177-181 (0.3)		59,35 59,60	8,51 8,62	C <sub>15</sub> H <sub>26</sub> O <sub>6</sub>	
(XVIII) + (XIX) (~2:1)	162-170 (0.3)		59,53 59,60	8,40 8,62	C <sub>15</sub> H <sub>26</sub> O <sub>6</sub>	
(XXI) + (XXII) (~4:1)	150-155 (0.25)		51,90 52,17	6,19 6,09	C <sub>10</sub> H <sub>14</sub> O <sub>6</sub>	
(XXIII)	158-164 (0.25)	1,4942	60,93 61,22	6,24 6,12	C <sub>15</sub> H <sub>18</sub> O <sub>6</sub>	2,1 m (2H, CH <sub>2</sub> ), 2,4 and 2,5 m (~2,5H, CH <sub>2</sub> COO), 2,9 m (~2H, CHCOO), 3,62 and 3,67 s (6H, CH <sub>3</sub> O), 4,3 m (~1,5H, CH <sub>2</sub> O), 4,7m (~0,2H, CH-O) 1,32 and 1,34 d (3H, CH <sub>3</sub> ), 2,6 m (2H, CH <sub>2</sub> COO), 3,1 m (1H, CHCOO), 3,60, 3,66 and 3,70 s (6H, CH <sub>3</sub> O), 5,4 m (1H, CH-O), 7,4 and 8,0 m (5H, C <sub>6</sub> H <sub>5</sub> )

\*Ester (XX) was identified by GLC on the basis of the appropriate standard, the synthesis of which is described in [8].



TABLE 5. Mass Spectra of 1:1 Adducts of Esters (I)-(VI) and Alkyl Maleates\*

Adduct	Mass numbers of ions (relative intensity, %)				
	M+	(M-OR)+	(M-OR')+ CH=COOR' CH <sub>2</sub> COOR'	characterizing the addition site of the alkyl maleate to the ester	others
(VIIa)	-	201 (51) *	243 (7)	259 (M-CH <sub>3</sub> ) + (0,6)	57 (100), 59 (73), 55 (66), 187 (61), 113 (51), 128 (47), 114 (39), 141 (36), 155 (27)
(VIIc)	274 (0,5)	215 (80) †	243 (6)	246 (M-C <sub>2</sub> H <sub>4</sub> ) + (2) 245 (M-C <sub>2</sub> H <sub>5</sub> ) + (3)	71 (100), 127 (78), 155 (68), 114 (59), 154 (58), 201 (52), 169 (50), 146 (49), 85 (45), 55 (26)
(IXc)	-	215 (60) †	243 (6)	259 (M-CH <sub>3</sub> ) + (0,8)	71 (100), 114 (75), 141 (52), 169 (51), 127 (38), 154 (33), 155 (30), 85 (32), 55 (33)
(VIIIc)	-	243 (40)	257 (20)	274 (M-C <sub>2</sub> H <sub>4</sub> ) + (1) 273 (M-C <sub>2</sub> H <sub>5</sub> ) + (2)	71 (100), 169 (81), 215 (67), 128 (61), 141 (42), 113 (41), 55 (20)
(Xc)	-	243 (57)	257 (35)	287 (M-CH <sub>3</sub> ) + (0,6)	71 (100), 128 (95), 169 (93), 215 (58), 113 (31), 55 (29)
(VIIIId)	-	271 (8)	257 (30)	246 (M-C <sub>4</sub> H <sub>9</sub> ) + (10)	128 (100), 55 (45), 95 (35), 197 (30), 183 (21), 151 (20), 229 (15), 169 (15)
(Xd)	-	271 (6)	257 (20)	287 (M-CH <sub>3</sub> ) + (0,3)	128 (100), 151 (40), 169 (32), 55 (30), 95 (18), 197 (14), 187 (12), 229 (6)
(XI)	-	271 (7)	257 (16)	274 (M-C <sub>2</sub> H <sub>4</sub> ) + (1) 273 (M-C <sub>2</sub> H <sub>5</sub> ) + (2)	128 (100), 55 (41), 183 (26), 169 (22), 95 (21), 151 (19), 197 (15), 81 (13)
(VIIe)	288 (0,6)	243 (54)	257 (42)	232 (M-C <sub>4</sub> H <sub>9</sub> ) + (15)	114 (78), 143 (76), 55 (47), 183 (45), 186 (37), 155 (35), 151 (31)
(IXe)	288 (0,4)	243 (10)	257 (9)	273 (M-CH <sub>3</sub> ) + (0,6)	114 (96), 151 (61), 183 (46), 143 (23), 55 (21), 123 (16), 155 (10), 169 (15)
(XIII)	288 (0,2)	-	257 (6)	273 (M-CH <sub>3</sub> ) + (0,6) 189 (M-C <sub>5</sub> H <sub>11</sub> , C=O) + (16) 99 (C <sub>5</sub> H <sub>11</sub> , C=O+) (100)	141 (59), 114 (55), 173 (34), 157 (30), 55 (24), 183 (17), 169 (11)
(XII)	288 (0,3)	243 (16)	257 (12)	260 (M-C <sub>2</sub> H <sub>4</sub> ) + (4) 259 (M-C <sub>2</sub> H <sub>5</sub> ) + (5)	114 (93), 169 (66), 183 (53), 210 (35), 143 (32), 123 (25), 55 (25), 151 (54), 155 (19)
(VIIIf)	316 (1)	285 (26)	285 (26)	218 (M-C <sub>7</sub> H <sub>14</sub> ) + (19)	114 (83), 55 (81), 59 (72), 128 (76), 187 (75), 186 (67), 171 (43), 127 (42), 210 (34), 211 (27)
(IXf)	316 (2)	285 (25)	285 (25)	301 (M-CH <sub>3</sub> ) + (4,5)	114 (56), 55 (53), 59 (31), 211 (25), 127 (19), 129 (13), 171 (13)
(XV)	288 (1)	-	257 (13)	273 (M-CH <sub>3</sub> ) + (2)	114 (98), 95 (97), 183 (88), 141 (82), 55 (74), 109 (57), 113 (56), 215 (53), 137 (52), 164 (35), 168 (33)
(XVI)	288 (0,7)	-	257 (3)	217 (M-C <sub>5</sub> H <sub>11</sub> ) + (10) 245 (M-CH <sub>3</sub> , C=O) + (7)	114 (97), 143 (59), 175 (58), 215 (57), 196 (48), 55 (41), 169 (39), 168 (32), 213 (35), 115 (34)
(XVII)	288 (1)	-	257 (2)	260 (M-C <sub>2</sub> H <sub>4</sub> ) + (1) 259 (M-C <sub>2</sub> H <sub>5</sub> ) + (1)	114 (99), 141 (88), 183 (78), 215 (68), 95 (66), 55 (65), 115 (41), 155 (37), 168 (36)
(XVIII)	-	-	271 (4)	287 (M-CH <sub>3</sub> ) + (4,5)	114 (100), 55 (31), 69 (21), 99 (16), 197 (16), 81 (14), 123 (7), 141 (6), 211 (4)
(XIX)	-	-	271 (8)	274 (M-C <sub>2</sub> H <sub>4</sub> ) + (1) 273 (M-C <sub>2</sub> H <sub>5</sub> ) + (2)	114 (100), 55 (32), 99 (29), 145 (26), 69 (21), 81 (18), 123 (16), 197 (13), 157 (8)

\*Also of the (M-CH<sub>2</sub>COOR')<sup>+</sup> ion. †Also of the (M-COOR')<sup>+</sup> ion.

as the internal standard. The molecular weights were determined by the ebullioscopic method in benzene on an SKB IOKh EP-75 instrument as described in [9].

Esters (Ia-f) and (II)-(VI), and the cp tert-butyl peroxide and AM, were purified by distillation.

Reaction of Esters (Ia-f) and (II)-(VI) with Alkyl Maleates (General Procedure). With efficient stirring, to 0.47 mole of the ester, either at reflux or heated to 180°, was added in 3-4 h a solution of 0.014 mole of tert-butyl peroxide and 0.07 mole of the AM in 0.23 mole of the ester. The mixture was heated for another 2 h, after which the excess ester and volatile reaction products were distilled off, and the 1:1 adducts were isolated by vacuum-distillation (Tables 1 and 3). The residue was analyzed as such. Adducts (VIIId), (Xd), (VIIIf), (IXf), (XV), and (XVIII) were isolated from the mixture of isomeric 1:1 adducts by repeated fractional distillation in vacuo. To work up the mixtures of isomeric 1:1 adducts we used a somewhat modified method, which is described below on the example of obtaining a mixture of (VIIIf) and (IX). With stirring, to 2.1 moles of ester (If) at 180° was added in 3 h a solution of 0.014 mole of tert-butyl peroxide and 0.07 mole of the AM in 0.23 mole of ester (If), and the mixture was heated for another 2 h. Then the described operation was repeated four times, each time adding 0.014 mole of the peroxide and 0.07 mole of the AM in 40 g of the reaction mixture. At the end of reaction we isolated 53 g of mixed isomeric 1:1 adducts by vacuum-distillation, the repeated fractional distillation of which gave 1.5 g of (VIIIf) and 1 g of (IXf).

The H-donor capacity of  $\text{CH}_3(\text{CH}_2)_n\text{COOMe}$  ( $n = 1-8$ ) toward tert-butoxyl radicals was determined by the method described in [2]. The obtained results are given in Table 2.

#### CONCLUSIONS

1. The reaction, initiated by tert-butyl peroxide, of the  $\text{C}_1\text{-C}_8$  alkyl esters of alkanolic acids, excluding the ethyl alkanoates, with alkyl maleates gives only the addition products at the acyl group of the ester, in which connection the propionates and isobutyrate react regioselectively at the  $\alpha\text{-C}$  atom, while the other esters react predominantly at the  $\omega\text{-1-C}$  atoms.

2. Hexyl acetate, octyl formate, and ethyl benzoate under analogous conditions add to alkyl maleates at the alkoxyl group (ethyl benzoate reacts regioselectively at the  $\alpha\text{-C}$  atom, while hexyl acetate and octyl formate react predominantly at the  $\omega\text{-1-C}$  atom).

3.  $\gamma$ -Butyrolactone and the alkyl maleate form the addition products at both the  $\alpha\text{-}$  and  $\gamma\text{-C}$  atoms of butyrolactone in an  $\sim 4:1$  ratio.

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