activated by o- and m-borates.

2. The borates, in contrast to phosphorus-containing activators, direct the reaction primarily towards the formation of linear trimers and tetramers of isoprene, namely, 3-methylene-7,11-dimethyl-1-trans-6,11-dodecatriene, 2,6,10-trimethyl-1-trans-3,5,10-dodecatriene, and 2,6,10,14-tetramethyl-1-trans-3,6,10,14-hexadecapentane.

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HOMOLYTIC ADDITION OF MALONIC AND SUCCINIC ACID ESTERS TO ALKYL MALEATES

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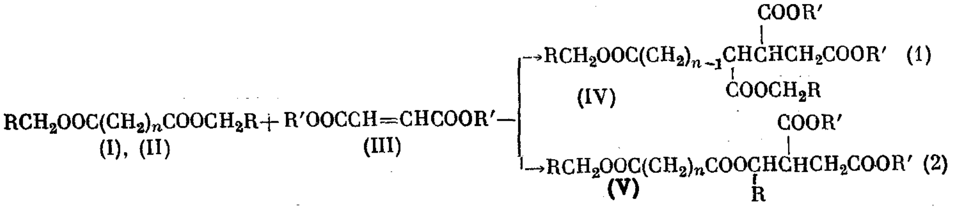
Esters add to unsaturated compounds by the action of peroxides and UV irradiation, forming 1:1 adducts and telomers [1]. 1-Alkenes have higher reactivity in this process than alkenes with an internal C=C bond [2,3]. Olefins of the type R'–CH=CH–X, in which R' is an alkyl group and X is an electron-acceptor functional group, occupy an intermediate position [4]. These studies indicate that the X groups at the C=C bond increase the reactivity of olefins in the homolytic addition of esters. They also lead us to expect that olefins of the type X–CH=CH–X will have enhanced reactivity in this reaction.

In the present work, the reaction of methyl and ethyl esters of malonic (I) and succinic (II) acids with the methyl and ethyl esters of maleic acid (III) (Table 1) initiated by tert-butyl peroxide was studied with the aim of supporting this hypothesis. The reactions were conducted at 145-180°C with a tenfold molar excess of esters of (I) and (II) relative to the alkyl maleate using 20 mole% peroxide relative to alkyl maleate. Under these conditions, the alkyl maleates undergo 85-100% conversion to 1:1 adducts with the esters of (I) and (II) and



$$\underset{(I),\ (II)}{RCH_2OOC(CH_2)_nCOOCH_2R} + \underset{(III)}{R'OOCCH{=}CHCOOR'} \rightarrow \underset{(IV)}{RCH_2OOC(CH_2)_{n-1}\underset{COOCH_2R}{\underset{|}{C}}H\overset{COOR'}{\overset{|}{C}}HCH_2COOR'}\ (1)$$

$$\rightarrow \underset{(V)}{RCH_2OOC(CH_2)_nCOO\underset{R}{\underset{|}{C}}H\overset{COOR'}{\overset{|}{C}}HCH_2COOR'}\ (2)$$

$n=1$, R=H, R'=CH_3 (a); $n=1$, R=H, R'=C_2H_5 (b); $n=1$, R=CH_3, R'=CH_3 (c)
$n=2$, R=H, R'=CH_3 (d); $n=2$, R=H, R'=C_2H_5 (e); $n=2$, R=CH_3, C_2H_5 (f).

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TABLE 1. Reaction of $CH_2(CO_2CH_2R)_2$ (I) and $RCH_2OOCCH_2CH_2COOCH_2R$ (II) with R'OOCCH=CHCOOR' in the Presence of tert-Butyl Peroxide at 180°C*

Run No.	Addend	RCH_2	R'	Conversion of alkyl maleate, %	1:1 adducts and their yield,‡ %		Telomeric products			Ratio of CH_3O and CH_3 signal intensities in the PMR spectrum	
							yield, %	molecular weight			
								found	calculated**	found	calculated**
1	(I)	CH_3	CH_3	–	(IVa), 4	–	70	398	420	–	–
2	(I)	CH_3	C_2H_5	–	(IVb), 4	–	58	506	476	0,50	0,50
3	(I)	C_2H_5	CH_3	85	(IVc), 6	(Vc), 2	56	421	448	2,0	2,0
4	(I)	C_2H_5	CH_3	–	(IVc), 2	(Vc), Traces	69	455	448	2,1	2,0
5†	(II)	CH_3	CH_3	82	(IVd), 21	(Vc), 5	53	–	–	–	–
6	(II)	CH_3	CH_3	95	(IVd), 21	(Vd), 5	54	446	434	–	–
7	(II)	CH_3	CH_3	100	(IVd), 45	(Vd), 10	44	–	–	–	–
8	(II)	CH_3	CH_3	100	(IVd), 10	(Vd), 2	76	425	434	–	–
9	(II)	CH_3	C_2H_5	100	(IVe), 23††	(Ve), 5	47	512	490	0,50	0,46
10	(II)	C_2H_5	C_2H_5	100	(IVf), 17	(Vf), 44	30	535	518	–	–

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*0.7 mole (I) or (II), 0.07 mole alkyl maleate, 0.014 mole peroxide; in run 7: 2 moles (II), 0.04 mole alkyl maleate, and 0.008 mole peroxide. The alkyl maleate was added over 3 h (runs 1-3, 5-7, 9, and 10) while in runs 4 and 8, it was mixed with (I) and (II) prior to onset of the reaction.

†Temperature 145°C.

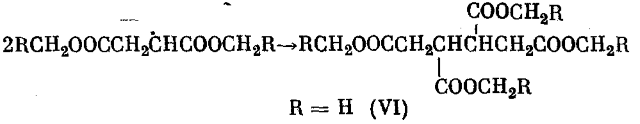
‡The yield of adducts (IV) and (V) was determined by gas–liquid chromatography relative to an internal standard. The yield of the telomeric adducts was derived relative to the initial alkyl maleate on the assumption that the only telomeric products are telomers (VII) and (VIII).

**The calculated values for the molecular weight and ratio of the CH_3O and CH_3 signal intensities are given for the corresponding telomers (VII) and (VIII). The calculation of the intensity ratio of these signals in run 9 was performed on the assumption that telomers (VIIe) and (VIIIe) are formed in a 4.6:1 ratio (the ratio of (IVe) and (Ve) in the reaction product).

††(IVd) in an amount 4% of (IVe) is formed in addition to (IVe) and (Ve).

to telomeric products. Ethyl malonate and alkyl succinates form two types of adducts with alkyl maleates as a result of the addition at the α-carbon atoms of the acid and alcoholic segments of the ester molecule.*

The structure of the acid and alcoholic segments of the addend significantly affect the ratio of adducts (IV) and (V). The dependence of the fraction of (V) in the total adducts (IV) and (V) on the structure of the addend is characterized by the following results: 0% for methyl malonate, 20% for methyl succinate, 25% for ethyl malonate, and 72% for ethyl succinate. The total yield of adducts (IV) and (V) from the alkyl malonates does not exceed 8%, while in the case of alkyl succinates, it may reach 60% (see Table 1, runs 3 and 10). Esters (IVd) and (IVf) are also obtained by the recombination of 1,2-dicarboalkoxyethyl radicals generated in the initiation and chain propagation steps (see general scheme).



$$2RCH_2OOCCH_2\dot{C}HCOOCH_2R \rightarrow RCH_2OOCCH_2\underset{\displaystyle COOCH_2R}{CH}\overset{\displaystyle COOCH_2R}{CH}CH_2COOCH_2R \quad (3)$$

R = H (VI)

Thus, as a result of the reaction of methyl succinate with ethyl malonate, in addition to the dimethyldiethyl esters of butane-1,2,3,4-tetracarboxylic acid (IVe), its tetramethyl ester (VI) forms in ∿4% of (IVe).† This ratio between (IVe) and (VI) indicates an insignificant contribution of reaction (3) in the formation of these compounds. Adduct (IVd) is formed as a mixture of approximately equal amounts of meso and racemic forms. The other adducts (IV) and (V) which contain two chiral centers also apparently are mixtures of diastereomers. In this regard, it is interesting to note that the dehydrodimerization of methyl succinate by the action of acetyl peroxide leads only to meso-(IVd) [5], while *d*- and *l*-(IVd) are obtained from methyl maleate under the action of manganese powder in HCl-saturated methanol [6].

The number of series of lower telomers (n = 2) which are formed in the homolytic reactions of unsaturated compounds with various addends, as a rule, corresponds to the number of types of 1:1 adducts obtained in these reactions. This condition and also the molecular weight determinations for the telomeric products of the alkyl maleates with the alkyl malonates and alkyl succinates and the ratio of their signal intensities in the PMR spectra (see Table 1) indicate that these products primarily consist of two 2:1 isomeric adducts, a hexaalkyl ester of the alkanehexacarboxylic acid (VII), and tetraalkyl ester of 5-carbalkoxyacyloxy-substituted alkanetetracarboxylic acid (VIII).

$$RCH_2OOC(CH_2)_{n-1}CH(COOCH_2R)—[—CH(COOR')CH(COOR')—]_2—H \quad (VII)$$
$$RCH_2OOC(CH_2)_nCOOCH(R)—[—CH(COOR')CH(COOR')—]_2—H \quad (VIII)$$

Their yield in most of the runs was from about 50 to 70%. Higher telomer homologs (3:1, 4:1 adducts, etc.) are virtually not formed. According to an approximate determination based on the PMR spectra, telomers (VII) and (VIII) are obtained in about the same ratio as the corresponding adducts (IV) and (V), except in runs 4 and 8, in which the ratio of (VII) to (VIII) was greater than the (IV):(V) ratio (see Experimental).

The highly pronounced tendency of the alkyl malonates and methyl succinate in the reaction with alkyl maleates to add to molecules of the monomer as seen from these results is unusual. This finding is the result, in our opinion, of the following factors: 1) the higher rate of addition of the adduct radicals $RCH_2OOC(CH_2)_{n-1}CH(COOCH_2R)CH(COOR')\dot{C}HCOOR'$ (A_1) and $RCH_2OOC(CH_2)_nCOOCH(R)CH(COOR')\dot{C}HCOOR'$ (B_1) to alkyl maleates relative to their removal of hydrogen atoms from the medium, 2) the rearrangement of the new adduct radicals (A_2) and (B_2) formed in this process into radicals (A_2^{per}) and (B_2^{per}) by intramolecular 1,5 hydrogen migration [7] and 3) the inability of the sterically hindered tertiary radicals (A_2^{per}) and (B_2^{per}) to add to alkyl maleate.

The formation of the major products of the homolytic reaction of alkyl malonates and alkyl succinates with alkyl maleates in light of these results and the generally accepted mechanism of free-radical processes of addition and telomerization may be given by Scheme 1. [Judging from the ratio of the decomposition products of tert-butyl peroxide (acetone and tert-butyl alcohol) (see Experimental Part), the initiation of the reaction occurs primarily by the action of methyl radicals.] The nucleophilic nature of these radicals [8] permits the assumption that their attack predominantly, and perhaps exclusively, is

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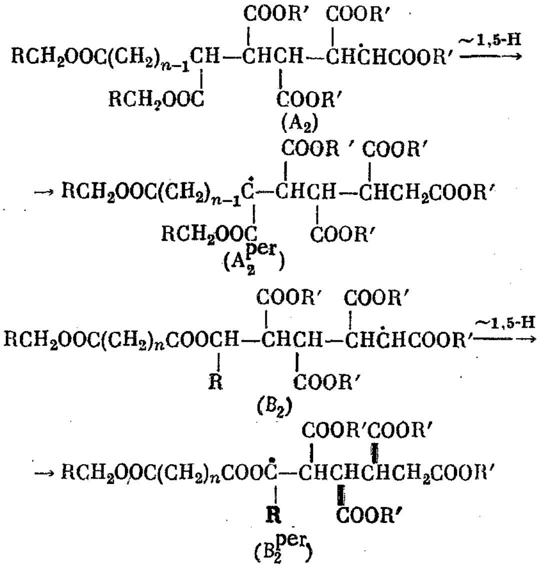
*Only adducts (IV) are obtained from methyl malonate.

†Transesterification of these esters under the conditions selected does not proceed.



$$\mathrm{RCH_2OOC(CH_2)_{n-1}\underset{RCH_2OOC}{CH}-\overset{COOR'}{CH}\underset{COOR'}{CH}-\overset{COOR'}{\dot{C}H}CHCOOR'} \xrightarrow{\sim 1,5\text{-}H}$$

$$(A_2)$$

$$\rightarrow \mathrm{RCH_2OOC(CH_2)_{n-1}\underset{RCH_2OOC}{\dot{C}}-\overset{COOR'}{CH}\underset{COOR'}{CH}-\overset{COOR'}{CH}CH_2COOR'}$$

$$(A_2^{per})$$

$$\mathrm{RCH_2OOC(CH_2)_nCOO\underset{R}{CH}-\overset{COOR'}{CH}\underset{COOR'}{CH}-\overset{COOR'}{\dot{C}H}CHCOOR'} \xrightarrow{\sim 1,5\text{-}H}$$

$$(B_2)$$

$$\rightarrow \mathrm{RCH_2OOC(CH_2)_nCOO\underset{R}{\dot{C}}-\overset{COOR'}{CH}\underset{COOR'}{CH}\overset{COOR'}{CH}CH_2COOR'}$$

$$(B_2^{per})$$

directed at the electrophilic centers of the ester molecule, namely the CH_2 groups of the acid segment of esters (I) and (II). Analogously, predominant attack on the alcoholic segment of esters (I) and (II) is expected for tert-butoxy radicals which have electrophilic nature.]

The structure and composition of adducts (IV) and (V) were confirmed by the PMR spectra, mass spectra, and elemental analysis results. The structure and composition of telomers (VII) and (VIII) were confirmed by the PMR spectra and molecular weight determinations (see Table 1).

Scheme 1

$$\mathrm{(CH_3)_3COOC(CH_3)_3 \rightarrow (CH_3)_3CO^{\cdot} \rightarrow \dot{C}H_3 + CH_3COCH_3}$$

$$\mathrm{RCH_2OOC(CH_2)_nCOOCH_2R + \dot{C}H_3 \rightarrow \underset{(A)}{RCH_2OOC(CH_2)_{n-1}\dot{C}HCOOCH_2R} + CH_4}$$

$$\mathrm{RCH_2OOC(CH_2)_nCOOCH_2R + (CH_3)_3CO^{\cdot} \rightarrow \underset{(B)}{RCH_2OOC(CH_2)_nCOO\dot{C}HR} + (CH_3)_3OH}$$

$$\mathrm{(A) + R'OOCCH{=}CHCOOR' \rightarrow (A_1) \qquad (B) + R'OOCCH{=}CHCOOR' \rightarrow (B_1)}$$

$$\mathrm{(A_1) + RCH_2OOC(CH_2)_nCOOCH_2R \rightarrow (IV) + (B) \qquad (B_1) + RCH_2OOC(CH_2)_nCOOCH_2R \rightarrow (V) + (B)}$$

$$\mathrm{(A_1) + R'OOCCH{=}CHCOOR' \rightarrow (A_2) \qquad (B_1) + R'OOCCH{=}CHCOOR' \rightarrow (B_2)}$$

$$\mathrm{(A_2) \xrightarrow{\sim 1,5\text{-}H} (A_2^{per}) \qquad (B_2) \xrightarrow{\sim 1,5\text{-}H} (B_2^{per})}$$

$$\mathrm{(A_2^{per}) + RCH_2OOC(CH_2)_nCOOCH_2R \rightarrow (VIII) + (B) \qquad (B_2^{per}) + RCH_2OOC(CH_2)_nCOOCH_2R \rightarrow (VIII) + (B)}$$

$$\mathrm{(B) + RCH_2OOC(CH_2)_nCOOCH_2R \rightarrow (A) + RCH_2OOC(CH_2)_nCOOCH_2R}$$

EXPERIMENTAL

The gas–liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with flame-ionization detector in a nitrogen current (25 ml/min). Columns: a) 2m × 3 mm with 10% DS-500 on Chromosorb W (0.2-0.25 mm), b) 1 m × 3 mm with 5% SE-30 on Chromosorb W (0.16-0.20 mm), and c) 2 m × 4 mm with 18% FFAP on Chromaton N-AW (0.16-0.20 mm). The mass spectra of the preparatively obtained compounds were obtained on a Varian MAT CH-6 spectrometer using a system for the direct introduction of the compound into the ion source at 70-eV ionizing electron energy and on a Varian MAT CH-111 spectrometer using chromatographic introduction (column b) at 50-eV ionizing electron energy. The PMR spectra were taken on a Varian DA-60-IL spectrometer (60 MHz) (with TMS internal standard). The molecular weights were determined by ebullioscopy in benzene on an ÉP-75 SKB IOKh instrument [9] according to the technique of Rappoport and Taits 10].

The pure-grade methyl and ethyl esters of malonic, succinic, and maleic acids were further purified by vacuum distillation. The sample of tert-butyl peroxide was obtained according to Miles and Surgenor [11].

Reaction of Alkyl Malonates (I) and Alkyl Succinates (II) with Alkyl Maleates (see Table 1, runs 1-10). General technique. To 0.47 mole ester (I) or (II) heated to 180°C, 0.014 mole tert-butyl peroxide and 0.07 mole alkyl maleate in 0.23 mole ester (I) or (II) were added over 3 h with stirring. The mixture was heated for 2 h at 180°C, and then the excess of (I) or (II) and the readily volatile reaction products were distilled out. Adducts (IV) or (V) or their mixture was then distilled under vacuum. Telomeric products consisting primarily of telomers (VII) and (VIII) were obtained in the residue. In runs 4 and 8, the peroxide was added as a solution in ethyl malonate and methyl succinate, respectively, and the alkyl maleates were mixed with the major amount of the addend prior to the onset of the reaction. In runs 5 and 7, a different reaction temperature and reagent ratio were used (see Table 1). The results of a study of the reaction products formed by gas—liquid chromatography, spectroscopy, and elemental analysis are given in Table 1 and below.

Tetramethyl Ester of Propane-1,1,2,3-tetracarboxylic Acid (IVa) (run 1). Mass spectrum:* 245 (5), $(M - CH_3O)^+$; 217 (24), $(M - CO_2CH_3)^+$; 212 (45), $(M - 2CH_3OH)^+$; 186 (41), $(M - OCH_3 - CO_2CH_3)^+$; 185 (37), $(M - CH_3OH - CO_2CH_3)^+$; 153 (100), —; 132 (33), —; 127 (10), —; 113 (13), —; 59 (43), $(CO_2CH_3)^+$. PMR spectrum of the residue:† 2.58 m (8, CH_2CO_2), 3.13 m (13, $CHCO_2$), 3.67 s (75, CH_3O), 4.05 d (4, O_2CCHCO_2).

Dimethyldiethyl Ester of Propane-1,1,2,3-tetracarboxylic Acid (IVb) (run 2). Mass spectrum: 273 (4), $(M - OCH_3)^+$; 259 (25), $(M - OC_2H_5)^+$; 245 (13), $(M - CO_2CH_3)^+$; 240 (19), $(M - 2CH_3OH)^+$; 231 (30), $(M - CO_2C_2H_5)^+$; 226 (31), —; 199 (50), —; 167 (46), —; 153 (100), —; 132 (42), —; 127 (43), —; 113 (42), —. PMR spectrum of the residue: 12.5 t (38, CH_3), 2.58 m (6, CH_2CO_2), 3.12 m (10, $CHCO_2$), 3.67 (19, CH_3O) and 4.03 q (27 (CH_2O) with overlapped signal from O_2CCHCO_2.

Diethyldimethyl Ester of Propane-1,1,2,3-tetracarboxylic Acid (IVc) and the Dimethyl Ester of 3-Carbethoxyacetyloxybutane-1,2-dicarboxylic Acid (Vc) (run 3). A mixture of esters (IVc) and (Vc) in 3:1 ratio was isolated, bp 132-137°C (0.2 mm Hg), Found: C 51.56; H 6.67%. Calculated for $C_{13}H_{20}O_8$: C 51.31; H 6.58%. PMR spectrum of the mixture of (IVc) and (Vc): 125 t (30, CH_3), 2.58 m (10, CH_2CO_2), 3.13 s + m (7, $O_2CCH_2CO_2$ and $CHCO_2$), 3.62 s (30, CH_3O), 4.09 q (21, CH_2O) with superposed signal from O_2CCHCO_2 and 5.10 m (2, CHO); residue: 1.25 d + t (21, CH_3), 2.60 m (8, CH_2CO_2), 3.16 s + m (15, $O_2CCH_2CO_2$ and $CHCO_2$), 3.63 and 3.64 s (42, CH_3O), 4.10 q (13, CH_2O) with superposed signal from O_2CCHCO and 5.09 (∿1, CHO). In the PMR spectrum from run 4, the following intensity ratios were observed: 21, 7, 13, 44, 14, and ∿0.7, respectively.

Tetramethyl Ester of Butane-1,2,3,4-tetracarboxylic Acid (IVd) (runs 5-8). A mixture was isolated containing meso and d,*l* forms of ester (IVd), bp 140-146°C (0.3 mm Hg), mp 56-58°C (from methanol). Found: C 49.90; H 6.09%. Calculated for $C_{12}H_{18}O_8$: C 49.65; H 6.21%. PMR spectrum: 2.58 m (4H, CH_2CO_2), 3.13 m (2H, $CHCO_2$), 3.57 s (6H, $CH_3O_2CCH_2$), 3.59 s (6H, CH_3O_2CCH). Mass spectrum: 259 (36), $(M - CH_3O)^+$; 258 (20), $(M - CH_3OH)^+$; 231 (4) $(M - CO_2CH_3)^+$; 199 (20), $(M - CH_3OH - CO_2CH_3)^+$; 166 (20), —; 139 (43), —; 115 (40), —; 114 (30), —; 101 (24), —; 59 (100), —; 55 (64), —.

A sample of 5 g ester (IVd) from run 7 was dissolved in 20 ml methanol and then petroleum ether was added to the solution. The mixture was allowed to stand for 24 h at ∿20°C. A yield of 1.15 g meso-(IVd), mp 74-76°C (see Alader and Schumacher [12]), was isolated from the precipitate (2.6 g) by repeated fractional crystallization from ether, selecting the first portions of crystal precipitate. Found: C 49.83; H 6.08%. Calculated for $C_{12}H_{18}O_8$: C 49.65; H 6.21%. The mother liquid obtained after separation of meso-(IVd) was evaporated and ∿2.4 g semisolid substance was obtained in the residue which hardened upon standing. Fraction crystallization of this material from methanol yielded 0.98 g d,*l*-(IVd), mp 63-64°C (see Alder and Schumacher [12]). Found: C 49.75; H 6.11%. Calculated for $C_{12}H_{18}O_8$: C 49.65; H 6.21%.

Dimethyl Ester of 3-(β-Carbomethoxypropionyloxy)propane-1,2-dicarboxylic Acid (Vd) (runs 5-8). Mass spectrum: 259 (11), $(M - OCH_3)^+$; 258 (5), $(M - CH_3OH)^+$; 231 (3), $(M - CO_2CH_3)^+$; 217 (24), $(M - CH_2CO_2CH_3)^+$; 199 (13), —; 198 (17), —; 175 (68), —; 159 (66), —; 158 (67), —; 143 (55), —; 127 (57), —; 126 (56), —; 116 (59), —; 115 (100), —; 114 (63), —; 99 (57), —; 87 (50), —.

The PMR spectrum of the residue from run 6: 2.56 s + m (17, CH_2CO_2), 3.12 m (12, $CHCO_2$), 3.63 s (69, CH_3O), 4.09 d (1.5, CH_2O). The ratio of the signals at 3.63 and 4.09 ppm corresponds to the (VIId):(VIIId) ratio = 4:1. The spectrum of the residue from run 8 is similar

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*The m/e values (relative intensity, %) and proposed assignment are given.

†The δ values, ppm, multiplicity (relative intensity, %, and assignment) are given.

to the above spectrum. The ratio of the signals at 3.63 and 4.09 ppm which corresponds to the (VIId):(VIIId) ratio in it is 6:1.

Dimethyldiethyl Ester of Butane-1,2,3,4-tetracarboxylic Acid (IVe) (run 9). Ester (IVe) was isolated, bp 137-142°C (0.2 mm Hg). Found: C 53.08; H 6.84%. Calculated for $C_{14}H_{22}O_8$: C 52.85; H 6.93%. PMR spectrum: 1.25 t (6H, CH_3), 2.56 m (4H, CH_2CO_2), 3.15 m (2H, $CHCO_2$), 3.63 s (3H, $\underline{CH}_3O_2CCH_2$), 3.65 s (3H, CH_3O_2CCH), 4.10 q (4H, CH_2O). Mass spectrum: 287 (19), $(M - CH_3O)^+$; 273 (40), $(M - C_2H_5O)^+$; 259 (16), $(M - CO_2CH_3)^+$; 215 (37), —; 213 (38), —; 212 (30), —; 187 (41), —; 153 (37), —; 141 (70), —; 140 (44), —; 139 (50), —; 127 (55), —; 126 (30), —; 115 (51), —; 114 (44), —; 113 (63), —; 99 (44), —; 59 (95), —; 55 (100), —.

Diethyl Ester of 3-(β-Carbomethoxypropionyloxy)propane-1,2-dicarboxylic Acid (Ve) (run 9). Ester (Ve) was isolated as a mixture with ester (IVe) in a 1:1 ratio, bp 142-150°C (0.2 mm Hg). Found: C 53.15; H 6.89%. Calculated for $C_{14}H_{22}O_8$: C 52.85; H 6.93%. PMR spectrum of the mixture: 1.25 t (27, CH_3), 2.56 s + m (23, $O_2CCH_2CH_2CO_2$ and CH_2CO_2), 3.13 m (7, $CHCO_2$), 3.62 and 3.63 s (20, $\underline{CH_3}O_2CCH_2$ and $\underline{CH_3}O_2CCH$), 4.10 q (23, CH_2O). PMR spectrum of the residue from run 9: 1.23 t (35, CH_3), 2.54 s + m (13, $O_2CCH_2CH_2CO_2$ and CH_2CO_2), 3.09 m (9, $CHCO_2$), 3.65 s (18, CH_3O), 4.06 q (25, CH_2O) with superposed signal from CH_2O.

Tetraethyl Ester of Butane-1,2,3,4-tetracarboxylic Acid (IVf) and Diethyl Ester of 3-(β-Carbethoxypropionyloxy)butane-1,2-dicarboxylic Acid (Vf) (run 10). A 1:2 mixture of esters (IVf) and (Vf) was isolated, bp 148-155°C (0.2 mm). Found: C 55.72; H 7.57%. Calculated for $C_{16}H_{26}O_8$: C 55.49; H 7.51%. PMR spectrum: 1.24 d + t (45, CH_3), 2.58 s + m (20, $O_2CCH_2CH_2CO_2$ and CH_2CO_2), 3.11 m (5, $CHCO_2$), 4.09 q (27, CH_2O), 5.13 m (2.5, CHO). Mass spectrum of ester (IVf): 301 (88), $(M - C_2H_5O)^+$; 273 (10), $(M - CO_2C_2H_5)^+$; 271 (29), —; 259 (5), $(M - CH_2CO_2C_2H_5)^+$; 255 (6), $(M - C_2H_5O - C_2H_5OH)^+$; 244 (9), $(M - 2C_2H_5OH)^+$; 227 (100), —; 226 (77), —; 199 (65), —; 181 (29), —; 180 (29), —; 153 (59), —; 128 (32), —; 127 (32), —; 125 (30), —; 55 (26), —. Mass spectrum of ester (Vf): 301 (13), $(M - C_2H_5O - C_2H_5O)^+$; 273 (1), $(M - CO_2C_2H_5)^+$; 259 (1), $(M - CH_2CO_2C_2H_5)^+$; 255 (1), $(M - C_2H_5O - C_2H_5OH)^+$; 254 (1), $(M - 2C_2H_5OH)^+$; 227 (17), —; 201 (23), —; 155 (33), —; 154 (26), —; 129 (100), —; 128 (25), —; 127 (37), —; 101 (83), —; 55 (28), —. The PMR spectrum of the residue from run 10: 1.25 t (47, CH_3), 2.55 s + m (14, O_2CCH_2, CH_2CO_2, and CH_2CO_2), 3.09 m (9, $CHCO_2$), 4.09 q (28, CH_2O), 5.12 m (1.7, CH–O). The ratio of the signals of 1.25 and 5.12 ppm corresponds to the (VIIf):(VIIIf) ratio in the residue which is equal to 1:2.

Decomposition of tert-Butyl Peroxide in Alkyl Esters of Malonic and Succinic Acids. A solution of 0.57 g peroxide in 17.67 g methyl malonate was heated for 24 h at 135°C in a sealed glass ampul. The gas–liquid analysis of the reaction mixture established the presence in it of only acetone. Traces of tert-butyl alcohol were not found. A similar result was obtained in the decomposition of the peroxide in ethyl malonate. In methyl succinate, the decomposition products of the peroxide were acetone and tert-butyl alcohol in the ratio ∿2.5:1.

CONCLUSIONS

1. The methyl and ethyl esters of maleic acid form 1:1 and 2:1 adducts with the methyl and ethyl esters of malonic and succinic acids in a reaction initiated by tert-butyl peroxide with high conversion (from 85 to 100%) and yield (from 75 to 100%).

2. Ethyl malonate and the alkyl succinates form two types of adducts with the alkyl maleates as a result of addition at the α-carbon atoms of the acid and alcohol segments of the ester. The addition of methyl malonate to alkyl maleates occurs only at the methylene group.

3. The alkyl malonates and methyl succinate predominantly add two molecules of alkyl maleate.

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THE PRODUCTION OF EPISULFONIUM COMPLEXES FROM PROPYLENE AND THE REGIOSELECTIVITY OF THEIR REACTIONS WITH NUCLEOPHILES

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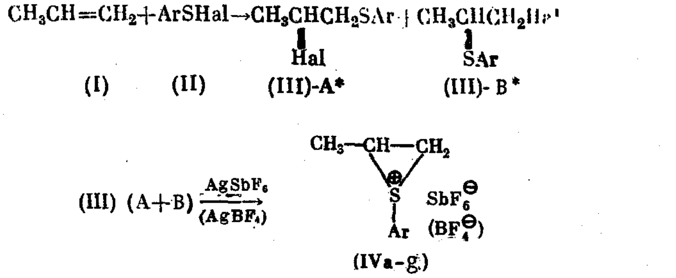
The aim of the present work was the production and characterization of episulfonium complexes (EC) from propylene (I) and also the study of the direction of their opening by various nucleophiles.

The synthesis of EC was carried out according to a scheme consisting of the production of the corresponding β-halothio ethers (III) from (I) and arylsulfene halides (II). The β-halothio ethers were then treated with $AgBF_4$ or $AgSbF_6$ in liquid sulfur dioxide or $C_2H_4Cl_2$—CH_2Cl_2 [1]. In the case of the bromium adducts (III, Hal = Br), the precipitation of AgBr proceeds readily and completely even at −50° to −40°C, while in the case of the chlorine adducts, complete precipitation was achieved only at −20° to −10°C over 30-60 min (Scheme 1). The EC (IVa-g) obtained were found to be rather stable in solutions at low temperature, which permitted their characterization by NMR spectroscopy and study of their reactions with nucleophiles.

Scheme 1



Ar=C_6H_5 (IVa), 4-$CH_3C_6H_4$ (IVb), 2,4,6-$(CH_3)_3C_6H_2$ (IVc), 4-ClC_6H_4 (IVd), 4-$CF_3C_6H_4$ (IVe), C_6F_5 (IVf), 2,4-$(O_2N)_2C_6H_3$ (IVg)

In the literature, the ^{13}C NMR spectrum of only one EC, namely, S-methyl-cis-di-tert-butylethylenesulfonium fluorosulfonate, has been described [2]. The ^{13}C signals for the methine carbon atoms in this EC were found shifted by 20.6 ppm downfield relative to the signals of the corresponding nuclei of cis-di-tert-butylethylene episulfide. The data in Table 1 indicate that an analogous change of the chemical shift of the EC studied in the present work is: ΔδC(1) 38.7-27.2 and ΔδC(2) 25.6-30.1 ppm. There is a double set of

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