### CONCLUSIONS

For the first time we have shown the feasibility of using pentafluoroperoxybenzoic acid for epoxidization of  $\alpha$ ,  $\beta$ -unsaturated esters, linear and cyclic dienes, for obtaining sulfoxides, sulfones, and N-oxides, and also for Baeyer-Villiger oxidation.

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# FREE-RADICAL ADDITION OF ESTERS TO ESTERS OF

#### CITRACONIC, ITACONIC, AND ACETYLENEDICARBOXYLIC

ACIDS

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The goal of our investigation was to compare the diethyl esters of citraconic acid (ECA) and itaconic acid (EIA) and also the dimethyl ester of acetylenedicarboxylic acid (MAA) with the dialkyl esters of maleic acid (AMA) in the reaction of free-radical addition with participation of esters as the addition agent, in particular the dimethyl esters of succinic acid (Ia), glutaric acid (Ib), and adipic acid (Ic).\* Furthermore, using MAA for the investigation, we could clarify the capacity of the adduct-radicals (A) (n = 2 or 3) to convert to cyclic products as a result of their rearrangement with 1,5- and 1,6-migration of hydrogen to the radicals(B) and cyclization of the latter by means of intramolecular addition at the C = C bond



<sup>\*</sup> The results of a study of reactions of esters with AMA are described previously [1-3].

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TABLE 1. Free-Radical Addition of Esters (Ia-c) and Xylene to ECA, EIA, and MAA (initiator: tert-butyl peroxide)\*

Addition agent	Ester of unsat. acid	Ester con- version, %	Reaction products and yields, % based on converted ester	Residue, g
(Ia)	ЕСА	18	(IIa), 66; (IIIa), 0,8 g	1,9
(Ia)	ЕІА	92	(IVa), 13; (VII), 17; (Va), 2.2; (VIa), 1	7,3 †
(Ic)	Е ІА	94	(IVc), 18; (VII), 25	7,7 †
(Ib)	МАА	95	(IXb), 33	6,6
(Ic)	МАА	96	(IXc), 45	5,2
o-Xylene	МАА	87	(XI), 33	4,8
m-Xylene	Е СА	19	(XII) ‡ ,78	2,1

\* Addition agent 0.7 mole, ester 0.07 mole, initiator 0.014 mole; temperature in the ester (Ia-c) experiments 180°C, in the xylene experiments 140°C; time 6 h.

<sup>†</sup> Average molecular weight of the residue in the reaction of (Ia) with EIA, 644; in reaction of (Ic) with EIA, 652.

‡ Diethyl ester of 1-methyl-2-(p-methylbenzyl) succinic acid.

Radical addition of esters (I) to ECA, EIA, and MAA was carried out at  $180^{\circ}$ C with a tenfold molar excess of the ester addition agent. As the initiator we used tert-butyl peroxide (TBP). Under these conditions, ECA reacted only to 18% completion, while EIA and MAA, similarly to AMA [1-3], reacted almost completely (92-95%) (Table 1). These results are evidence for the substantial steric effect of the CH<sub>3</sub> group in ECA on addition of radicals to this ester, which is also indicated by data on the relative rate of addition of alkyl radicals to citraconic and maleic anhydride [4].

In the product of reaction between dimethylsuccinate (Ia) and ECA, we identified the dimethyldiethyl ester of pentane-1,2,3,4-tetracarboxylic acid (IIa) (adduct 1:1) and the tetramethyl ester of butane-1,2,3,4-tetracarboxylic acid (IIa) – the product of recombination of 1,2-(dimethyoxycarbonyl)ethyl radicals (C) (see Table 1).



As a result of homolytic addition of (Ia) and dimethyl adipate (Ic) to EIA, esters of pentane-1,2,4,5tetracarboxylic acid (IVa) and heptane-1,2,4,7-tetracarboxylic acid (IVc) are formed:



In the product of reaction of (Ia) with EIA, besides the adduct (IVa) we observe the dimethyl ester of itaconic acid (Va), the tetramethyl (VIa) and tetraethyl (VII) esters of pentane-1,2,4,5-tetracarboxylic acid (see Table 1). The formation of these compounds probably proceeds according to the scheme given below, which is considered in detail in [5].





 $X = CO_2Et$ ,  $Y = CO_2Me$ .

The homolytic reaction of dimethyl glutarate (Ib) and dimethyl adipate (Ic) with MAA leads respectively to the tetramethyl ester of 2-pentene-1,2,3,5-tetracarboxylic acid (IXb) and 2-hexene-1,2,3,6-tetracarboxylic acid (IXc) — the isomerization product of the initially obtained adducts (VIIIb, c)



Similar isomerization was observed earlier in the reaction of free-radical addition of malonic ester to 1hexene and propargyl acetate [6]. Cyclic products derived from radical (B) are not observed. We also could not obtain cyclic products by reaction of MAA with o-xylene, although in this case the rearrangement of the initially formed adduct-radical (D) to radical (E) and homolytic cyclization of the latter were much more probable than for radicals (A) and (B)



The principal products of this reaction proved to be the Z and E isomers of the o-methyldimethyl ester of o-methylbenzylidenesuccinic acid (XI)

$$o-CH_{3}C_{6}H_{4}CH_{3} \xrightarrow{MAA} o-CH_{3}C_{6}H_{4} \xrightarrow{CO_{2}Me} (X) \xrightarrow{Isomerization} o-CH_{3}C_{6}H_{4} \xrightarrow{CO_{2}Me} (XI)$$

The structure of (XI) is confirmed by PMR and mass spectra (Table 2). In the PMR spectrum, there were no signals from protons of the CH<sub>2</sub> group adjacent to the aryl and the C = C bond ( $\delta \sim 3.4$  ppm [7]) and the methine proton of the C=CHCO<sub>2</sub>Me group ( $\delta 5.8-6.8$  ppm [8]), which indicates complete isomerization of the initially obtained dimethyl ester of o-methylbenzylethylene-1,2-dicarboxylic acid (X) to (XI). The conclusion concerning the formation of the ester (XI) in the Z and E forms is based on the presence in the PMR spectrum of singlet signals  $\delta 2.22$  and 2.31 ppm, corresponding to the signals of protons of the CH<sub>3</sub> in the  $\beta$ -substituted cisand trans-o-methylstyrenes [9]. We must assume by analogy that the esters (IXb) and (IXc) are also formed as a mixture of Z and E isomers. The structure of the remaining reaction products is confirmed analogously to compound (XI) (see Tables 2 and 3).

An important distinguishing characteristic of homolytic addition of esters (Ia-c) to ECA, EIA, and MAA compared with the analogous reactions of (Ia-c) with AMA is the high regioselectivity – the formation of a new C-C bond between esters (Ia-c) and ECA, EIA, and MAA occurs practically exclusively between the  $\alpha$  C atom of the ester of the alkanedicarboxylic acid and the least substituted C atom of the C=C bond of the ester of the unsaturated acid. Products of addition relative to the methoxyl group of esters (Ia-c) are not observed. In reactions of the same esters with AMA, the relative yield of such adducts reaches 15-25% [2]. On addition of (Ia-c) to ECA and EIA, this characteristic is probably due to the fact that their tertiary adduct-radicals, in contrast to the secondary adduct-radicals formed in the reaction of (Ia-c) with AMA, are not able to abstract an H atom from the COOCH<sub>3</sub> group.

TABLE 2. Mass and PMR Spectra of the Reaction Products

Com-	Mass spectrum: m/z, proposed assignment	PMR spectrum
pound	(rel, intensity)	(δ, ppm)
(IIa)	317, $(M-CH_3)^+$ (1,5); 301, $(M-CH_3O)^+$ (29); 287, $(M-C_2H_5O)^+$ (61); 273 $(M-COOCH_3)^+$ (17); 259 (11); 227 (100); 226 (59); 213 (44); 199 (58); 167 (51); 146, $(CH_3OOCCH_2CH=C(OH)OCH_3)^+$ (29); 141 (44); 127 (41);115 (63); 59 (58); 55 (44)	
(IVa)	301, (MCH <sub>3</sub> O) <sup>+</sup> (25); 287, (MC <sub>2</sub> H <sub>5</sub> O) <sup>+</sup> (51); 273, (MCOOCH <sub>3</sub> ) <sup>+</sup> (7); 259, (MCOOC <sub>2</sub> H <sub>5</sub> ) <sup>+</sup> (13); 255 (64); 254 (75); 241 (49); 227 (88); 243 (52); 199 (63); 187 (28); 174, (C <sub>2</sub> H <sub>5</sub> OOCCH <sub>2</sub> CH=C(OH)OC <sub>2</sub> H <sub>5</sub> ) <sup>+</sup> (25); 167 (75); 146, (CH <sub>3</sub> OOCH <sub>2</sub> CH=C(OH)OCH <sub>3</sub> ) <sup>+</sup> (27); 139 (61); 128 (88); 114 (400); 55 (51)	$\begin{array}{c} {\rm 4,2t} \ (6{\rm H},\ C{\rm H}_3),\ {\rm 1,8m} \\ (2{\rm H},\ C{\rm H}_2),\ 2.6\ m(4{\rm H},\ C{\rm H}_2{\rm OO}),\ 2.9\ m(2{\rm H},\ C{\rm H}_2{\rm OO}),\ 3.59\ ;\ 3.61c \\ (6{\rm H},\ C{\rm H}_3{\rm O}),\ 4.01\ ;\ 4.03m \\ (4{\rm H},\ C{\rm H}_2{\rm O}) \end{array}$
(IVc)	329, $(MCH_3O)^+$ (8); 315, $(MC_2H_5O)^+$ (20), 301, $(MCOOCH_3)^+$ (7); 287, $(MCOOC_2H_5)^+$ (4); 283 (8); 241 (14); 195 (17); 187 (19); 174, (C-H_5OOCCH_2CH= C(OH)OC_2H_5)^+ (26); 149 (29); 141 (28); 128 (45); 144 (33); 59 (59); 55 (100)	$\begin{array}{l} 1,2t \ (6H,\ CH_3),\ 1,4\ m(4H,\\ CH_2),\ 1.8\ m(2H,\ CH_2),\\ 2,6\ m\ (4H,\ CH_2CO),\\ 2,9\ m\ (2H,\ CHCOO),\\ 3,60\ ;\ 3,62\ s\ (6H,\ CH_3O),\\ 4,01\ ;\ 4,02\ m(4H,\ CH_2O). \end{array}$
(VIa)	273, (MCH <sub>3</sub> O) <sup>+</sup> (7); 245, (MCOOCH <sub>3</sub> ) <sup>+</sup> (3); 244, (MCH <sub>3</sub> OHCH <sub>3</sub> O) <sup>+</sup> (10); 240, (M2CH <sub>3</sub> OH) (7); 213 (11); 199 (8); 185 (13); 181 (12); 167 (11); 159 (7); 153 (17); 146, (CH <sub>3</sub> OOCCH <sub>2</sub> CH=-C(OH)OCH <sub>3</sub> ) <sup>+</sup> (7); 159 (22); 127 (21); 114 (28); 1C1 (14); 59 (100); 55 (49)	1.8t (2H, CH <sub>2</sub> ), 2.5 m (4H, CH <sub>2</sub> COO), 2.9 m (2H, CHCOO), 3.61; 3.63s (12H, CH <sub>3</sub> O)
(VII)	345, $(M-C_2H_3O)^+$ (43); 287, $(M-COOC_2H_5)^+$ (8); 273, $(M-CH_2COOC_2H_5)^+$ (21); 269, $(M-C_2H_3O-$ $-C_2H_3OH)^+$ (7); 268, $(M-2C_2H_3OH)^+$ (57); 241 (51); 227 (43); 213 (49); 195 (56); 187 (36); 174, $(C_3H_0OCCH_2CH=C(OH)OC_2H_5)^+$ (29); 167 (42); 144 (56); 128 (100); 113 (35); 100 (34); 55 (28)	$\begin{array}{c} 1,2 t (12H, CH_3), 1,8 t \\ (2H, CH_2), 2,6 m (4H, \\ CH_2COO), 2,9 m (2H, \\ CHCOO), 4,0 i ; 4,0 3 m \\ (8H, CH_2O) \end{array}$
(IXb)	302, (M <sup>+</sup> ) (2); 274, (M $-CH_3O$ ) <sup>+</sup> (27); 243, (M $-COOCH_3$ ) <sup>+</sup> (9); 229, (M $-CH_2OOCH_3$ ) <sup>+</sup> (4); 215, (M $-CH_2CH_2COOCH_3$ ) <sup>+</sup> (3); 240 (22); 183 (22); 151 (42); 115 (44); 100 (54); 87 (61); 59 (100); 55 (77)	2,5 <sup>m</sup> (4H, CH <sub>2</sub> ), 3,63; 3,67s (12H, CH <sub>3</sub> O), 3,84; 3,86s (2H, CH <sub>2</sub> )
(IXc)	$ \begin{cases} 316, (M)^+ (1); 285, (M-CH_3O)^+ (18); 257, (M-COOCH_3)^+ (5); 243, (M-CH_4COOCH_3)^+ (6); 224, (M-COOCH_3)^+ (2); 215, (M-(CH_2)_3, (M-COOCH_3)^- (2); 197 (21); 165 (28); 151 (17); 137 (27); 114 (32); 59 (100); 55 (74) \end{cases} $	$\begin{array}{c} 1.8m(2H,\ CH_3),\ 2.5m\\ (4H,\ CH_2),\ 3.56\ ;\ 3.61s\\ (12H,\ CH_3O),\ 3.69\ ;\ 3.71s\\ (2H,\ CH_2) \end{array}$
(XI)	$ \begin{bmatrix} 248, (M^+) & (10); & 217, (MCH_3O)^+ & (13); & 216, (MCH_3OH)^+ & (23); & 188, (MCCOCH_3)=OH)^+ & (28); & 185, (MCH_3O-CH_3OH)^+ & (8); & 174, (MCH_2C(OCH_3)=OH)^+ & (12); & 156 & (17); & 145 & (21); & 124 & (100); \\ OH)^+ & (12); & 156 & (17); & 145 & (21); & 128 & (100); \\ 114 & (52); & 104 & (37); & 91 & (31); & 77 & (32); & 59(33) \end{bmatrix} $	$ \begin{vmatrix} 2,22 & ; 2,3! & (3H, CH_3Ar), \\ 3,59 & 3,63 & ; 3,69s & (12H, \\ CH_3O), & 3,76 & ; 3,85s & (2H, \\ CH_2), & 6,95m & (5H, C_6H_4; \\ ArCH=) \end{vmatrix} $
(XII)	$ \begin{bmatrix} 292, (M^+) (10); 247, (M-C_2H_5O)^+ (15); 218, (M-C_2H_5O)^+ (15); 218, (M-C_2H_5)^- OH)^+ (34); 201 (45); 191 (98); 173 (52); 145 (99); 105, (CH_3C_6H_4CH_2)^+ (100); 77 (21); 74 (30); 55 (9) \end{bmatrix} $	$ \begin{array}{c} 1,2 \mbox{ m} (9H, \mbox{ CH}_3), 2,22 \mbox{ s} \\ (3H, \mbox{ CH}_3 \mbox{ Ar}), 2,5-2,9 \mbox{ m} \\ (4H, \mbox{ CH}_2 \mbox{ Ar}); \mbox{ CHCOO}), \\ 4,01; \mbox{ 4,03 \mbox{ m} (4H, \mbox{ CH}_2 \mbox{ O})}, \\ 6,9 \mbox{ m} (4H, \mbox{ CH}_2 \mbox{ H}_1) \end{array} $

The capacity of esters (Ia-c) to form adducts with EIA and MAA is increased in proportion to the increase of the number of  $CH_2$  groups in (Ia-c). An analogous dependence was observed in reactions of esters (Ia-c) with AMA [2]. It was proposed [2] that the latter is connected with the electrostatic repulsion by the ester groups of the electrophilic radicals when they abstract H atoms from esters (Ia-c), which decreases with an increase in the length of the hydrocarbon chain of the acyl part of the esters. The shielding effect of the COOR groups during attack of esters of alkanedicarboxylic acids by radicals is noted in [10]. For similar reasons, the capability of esters (Ia-c) to form adducts with EIA and MAA probably increases in the order (Ia) < (Ib) < (Ic).

As an acceptor of radicals generated from ester (Ia) and p-xylene,\* EIA is substantially less effective than derivatives of maleic acid [2, 4]; this is apparently due primarily to the sharp retardation of the step of radical addition to ECA of the induced substitution of one of the H atoms with the C = C bond of AMA by the  $CH_3$  group. The low rate of addition of radicals to the trisubstituted C = C bond might be one of the reasons for the absence of cyclic products in the reaction of esters (Ib) and (Ic) with MAA.

<sup>\*</sup> We chose p-xylene as the addition agent in the ECA reaction in order to estimate the acceptor ability of the trisubstituted C = C bond in ECA in addition of a benzyl-type radical, in which the radical center is less spatially shielded by the substituents than the secondary radicals (C).

Compound	mp,°C	n:•D	Empirical formula	Found/calcu- lated, %/%	
				C	н
(IVa)	140-142(0,2)	1,4553	C15H24O8	54,47	7,41
(IVc)	173-178 (0,25)	1,4572	$C_{17}H_{28}O_8$	<u>56,92</u> 56,67	7,25 <u>7,77</u> 7,78
(VIa)	157–158 (0,3)	1,4579	$C_{13}H_{20}O_8$	<u>51,63</u> 51.32	6,52
(VII)	148-150 (0,2)	1,4528	$C_{17}H_{28}O_8$	$\frac{56,67}{56,67}$	7,61
(IXb)	146-148(0,3)	1,4663	$C_{13}H_{18}O_8$	$\frac{51,96}{51.65}$	<u>6,15</u> 5.96
(IXc)	165-467 (0,4)	1,4666	$C_{14}H_{20}O_8$	$\frac{53,11}{53,16}$	<u>6,28</u> 6,33
(XI)	122125 (0,3)	1,5268	C14H16O4	$\tfrac{67,86}{67,74}$	<u>6,31</u> 6,45
(XII)	118-120(0,2)	1,4899	$C_{17}H_{24}O_4$	$\frac{69,50}{69,86}$	$\tfrac{-7,92}{-8,22}$

TABLE 3. Properties of the Principal Products from Reaction of Esters (Ia-c) and Xylenes with ECA, EIA, and MAA

#### EXPERIMENTAL

GLC analysis was performed on the LKhM-8MD chromatograph with a flame-ionization detector in a flow of nitrogen (30 ml/min); columns: a)  $2 \text{ m} \times 3 \text{ mm}$  with 10% DS-550 on Chromosorb W (0.20-0.25 mm); b)  $2 \text{ m} \times 3 \text{ mm}$  with 15% PEGS on Chromosorb W (0.20-0.25 mm); c)  $3 \text{ m} \times 3 \text{ mm}$  with 12% PEGS on Chromaton N (0.20-0.25 mm); d)  $1 \text{ m} \times 3 \text{ mm}$  with 5% SE-30 on Chromaton N (0.16-0.20 mm). Mass spectra are obtained on a Varian MAT CH-6 instrument with direct injection of material into the ion source at 70 eV or using the chromatographic injection in the Varian MAT CH-111. The PMR spectra were taken on a Tesla BS-497 instrument (100 MHz), internal standard TMS.

Dimethyl succinate (Ia), dimethyl glutarate (Ib), dimethyl adipate (Ic), and the diethyl ester of itaconic acid (EIA) - cp grade - were additionally purified before use by distillation. The diethyl ester of citraconic acid (ECA) and the dimethyl ester of acetylenedicarboxylic acid (MAA) are obtained from citraconic anhydride and the dicalcium salt of acetylenedicarboxylic acid [11].

Reaction of Dimethyl Succinate (Ia) with ECA. To 0.47 mole of ester (Ia) heated to 180°C, after 4 h we added with effective mixing a solution of 0.014 mole of tert-butyl peroxide and 0.07 mole of ECA in 0.23 mole of ester (Ia). The mixture was heated for another 2 h, cooled, and the content of unconverted ECA and the reaction products in the mixture was determined by GLC. Then the excess of ester (Ia) was distilled, and from the residue by vacuum distillation we isolated a mixture of esters (IIa) and (IIIa), which were identified without separation from the mixture by chromatography-mass spectrometry and GLC using the relevant data.

According to an analogous technique, we accomplished the reaction of p-xylene with ECA (see Table 1). Additional introduction into the reaction mixture of a solution of 0.014 mole peroxide in 30 ml p-xylene at 140°C after 4 h allowed us to increase the conversion of ECA to 41%. The yield of ester (XII) relative to converted ECA in this case decreased to 62%.

We carried out the reactions of esters (Ia) and (Ic) with ECA and esters (Ib), (Ic) and o-xylene with MAA in an analogous manner. The properties and spectra of the reaction products obtained are given in Tables 2 and 3. The esters (Va) and (VIa) are identified by GLC from the relevant data. The data corresponding to ester (VIa) are obtained by hom olytic addition of ester (Ia) to the dimethyl ester of itaconic acid according to the technique described above.

#### CONCLUSIONS

1. A new C-C bond on homolytic addition of dimethyl esters of succinic, glutaric, and adipic acids to the dimethyl or diethyl ester of citraconic, itaconic, and acetylenedicarboxylic acids is formed between the  $\alpha$ -C atom of the acyl part of the ester of the alkanedicarboxylic acid and the least substituted C atom of the C=C bond of the ester of the unsaturated acid.

2. As an acceptor of radicals generated from esters of alkanedicarboxylic acids, the ester of citraconic acid is substantially less effective than the esters of maleic, itaconic, and acetylenedicarboxylic acids. The latter are close to one another in capability of forming addition products with esters of succinic, glutaric, and adipic acids.

3. The principal products of homolytic reaction of dimethyl esters of glutaric and adipic acids with the dimethyl ester of acetylenedicarboxylic acid are respectively the tetramethyl esters of 2-pentene-1,2,3,5-tetra-carboxylic acid and 2-hexene-1,2,3,6-tetracarboxylic acid.

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# RADICAL ARYLATION OF THIOSEMICARBAZIDE AND ACETONE THIOSEMICARBAZONE BY ARYLDIAZONIUM

BOROFLUORIDES

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We have reported [1-3] the first evidence that aryl radicals generated by thermal decomposition of phenylazotriphenylmethane or N-nitrosoacetanilides arylate thiourea and N, N'-diphenylthiourea to form S-arylisothiouronium bases



The yield of these compounds reached 56% from N, N-diphenylthiourea but did not exceed  $\sim 1\%$  from thiourea.

In the work reported here we have examined the radical arylation of analogs of thiourea – thiosemicarbazide (TSC) and acetone thiosemicarbazone (ATSC) – using different free-radical sources, phenyldiazonium (PD) and p-nitrophenyldiazonium (NPD) borofluoride. These borofluorides arylate TSC and ATSC to form S-arylisothiosemicarbazides and their derivatives. However, PD borofluoride arylates TSC and ATSC only in the presence of  $CuCl_2 \cdot 2H_2O$ , pointing to the radical character of this arylation. NPD borofluoride arylates TSC and ATSC in the absence of  $CuCl_2 \cdot 2H_2O$ . To clarify the nature of arylation in this case we have examined the interaction of NPD borofluoride with TSC by ESR using a spin trap, 2-methyl-2-nitrosopropane (MNP). When equimolar quantities of NPD borofluoride and TSC in benzene are mixed in the presence of MNP at 25°C, the ESR

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