STRUCTURAL ORIENTATION IN DIENE CONDENSATIONS OF 1-ALKYL-1,3-BUTADIENES WITH UNSYMMETRIC DIENOPHILES*

I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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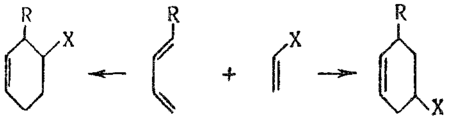
The question of structural orientation in the diene synthesis, as a part of the more general question of the mechanism of this reaction, has attracted the attention of many investigators. In the diene condensations of 1-alkyl-1,3-butadienes two structural isomers can be formed, i.e., the ortho and meta forms:



For a long time it was considered that in such reactions only the ortho-isomer is formed. However, in 1947 in the condensation of piperylene with acrylonitrile, Frank, Emmick, and Johnson [1] proved the presence of a small amount of meta-isomer in the mixture of adducts. Later, this matter was studied in detail in our laboratory [2], when it was proved fairly rigorously that in the condensations of piperylene with acrylonitrile, methyl acrylate, methyl methacrylate, styrene, and crotonic acid mixtures of both possible adducts were formed and the content of meta-isomer was 10-15%. The presence of about 15% of meta-isomer was found also by Petrov and Sopov [3] in the product of the condensation of piperylene with acrolein. Until recently there has been scarcely any study of structural orientation in the diene condensations of other 1-alkyl-1,3-butadienes; there is only an investigation by Alder [4] in which it was proved that about 25% of meta-isomer is formed in the condensation of 1-t-butyl-1,3-butadiene (5,5-dimethyl-1,3-hexadiene) with acrylic acid.

With the object of making a systematic investigation of structural orientation in the diene synthesis as a function of the sizes of the substituents in the diene and dienophile, as dienes we took 1-methyl-, 1-isopropyl-, 1-butyl-, and 1-t-butyl-1,3-butadienes [trans-piperylene, 5-methyl-1,3-hexadiene, 1,3-octadiene, and 5,5-dimethyl-1,3-hexadiene] and as dienophiles we took esters of acrylic, methacrylic, and 2-isopropylacrylic acids. The diene condensations were carried out by heating a mixture of diene and dienophile in a steel ampule at 200° for 2-15 hr. The compositions of the mixtures of adducts formed in the condensation of 1-alkyl-1,3-butadienes with methyl acrylate were established from the scheme given below.

The mixture of adducts (I) and (II) was dehydrogenated over palladized charcoal (15% Pd), and the dehydrogenation products (III) and (IV) were hydrolyzed with methanolic sodium hydroxide. Oxidation of the resulting aromatic acids (V) and (VI) with dilute nitric acid in an autoclave [2] led to a mixture of phthalic and isophthalic acids. On the basis of the difference in solubility of these acids in hot water** their relative amounts

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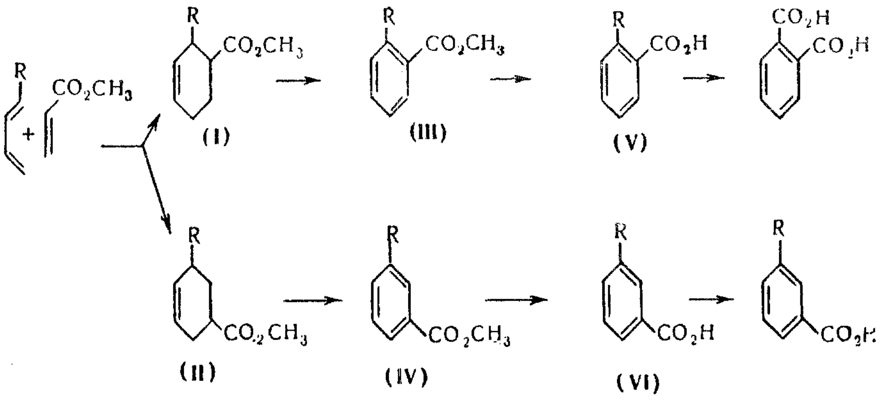
*The work was completed after the death of I. N. Nazarov.

**At 99° 100 g of water dissolves 18 g of phthalic acid, but only 0.2 g of isophthalic acid.

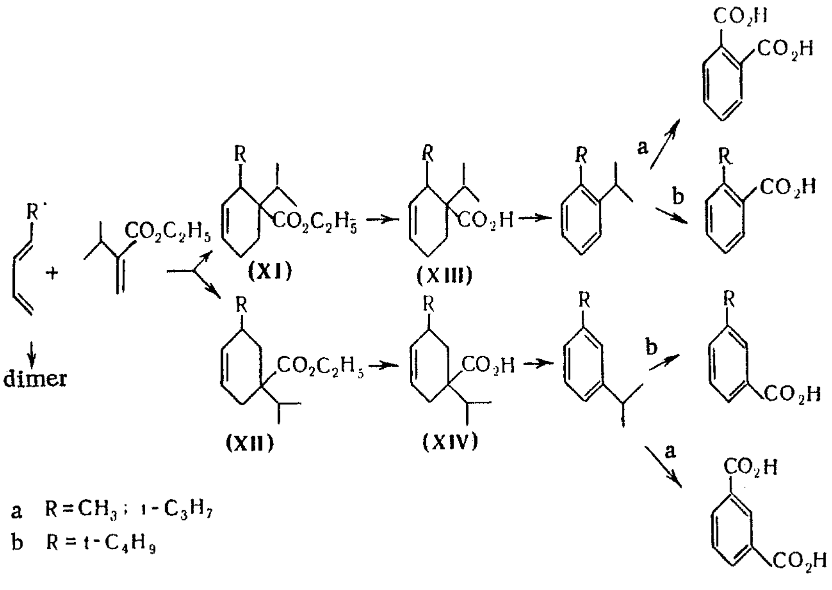


$R = CH_3; i\text{-}C_3H_7; C_4H_9; t\text{-}C_4H_9$

were determined, and these corresponded to the relative amounts of ortho- and meta-isomers (I) and (II) in the original mixture of adducts. In the case of 5,5-dimethyl-1,3-hexadiene, (V) and (VI) ($R = t\text{-}C_4H_9$) were separated directly by crystallization. The results are given in the table.

With the object of studying the effect of temperature on the relative amounts of structural isomers formed, we investigated the condensation of piperylene with methyl acrylate at various temperatures. It was found that at 20° (one year) the ratio of the amounts of ortho- and meta-adducts is 18 : 1, whereas at 400° (in a flow system) it is 3.7 : 1. Comparing these results with those for the condensation at 200° (ortho : meta = 6.8 : 1; see table), we may conclude that with rise in the condensation temperature the relative amount of the meta-isomer in the mixture of adducts formed increases. We established the same relation earlier [5] for the case of the condensation of isoprene with the same dienophile.

For the condensation of 1-alkyl-1,3-butadienes with methyl methacrylate, the relative amounts of the adducts (VII) and (VIII) were determined in accordance with the following scheme:



a $R = CH_3; i\text{-}C_3H_7$

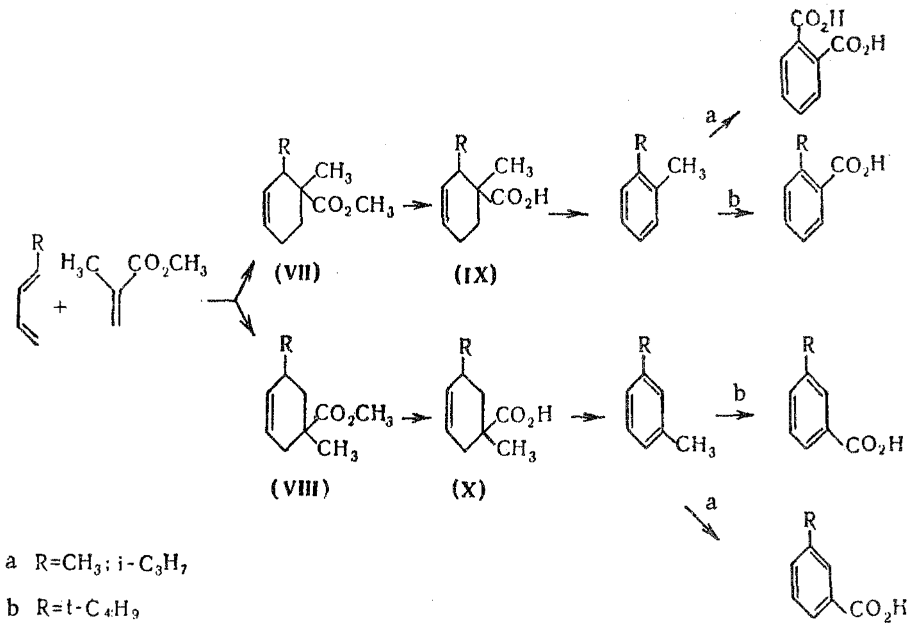
b $R = t\text{-}C_4H_9$

By hydrolysis of the adducts (VII) and (VIII) with methanolic sodium hydroxide we obtained the acids (IV) and (X), whose dehydrogenation over palladized charcoal gave a mixture of aromatic hydrocarbons, which were oxidized with dilute nitric acid under pressure. In the case of piperylene and 5-methyl-1,3-hexadiene, oxidation gave mixtures of phthalic and isophthalic acids [Scheme (a)], which were separated by selective extraction with hot water, and in the case of 5, 5-dimethyl-1,3-hexadiene [Scheme (b)] it gave a mixture of o- and m-t-butylbenzoic acids, which were separated by fractional crystallization.

Relative Amounts of o- and m-Adducts Formed in the Condensation of 1-Alkyl-1,3-butadienes with Esters of α-Substituted Acrylic Acids

Diene	Dienophile		
	$CH_2{=}CH{-}CO_2CH_3$	$CH_2{=}\overset{CH_3}{C}{-}CO_2CH_3$	$CH_2{=}\overset{CH(CH_3)_2}{C}{-}CO_2C_2H_5$
$CH_3{-}CH{=}CH{-}CH{=}CH_2$	6,8 : 1	4,9 : 1	2,5 : 1
$(CH_3)_2CH{-}CH{=}CH{-}CH{=}CH_2$	5 : 1	3,1 : 1	2,4 : 1
$C_4H_9{-}CH{=}CH{-}CH{=}CH_2$	5,1 : 1	—	—
$(CH_3)_3C{-}CH{=}CH{-}CH{=}CH_2$	4,1 : 1	2,6 : 1	0,9 : 1

The condensation of 1-alkylbutadienes with ethyl 2-isopropylacrylate [ethyl 3-methyl-2-methylenebutyrate] gave mixtures of the adducts (X) and (XII), which in the case of 5-methyl- and 5,5-dimethyl-1,3-hexadienes contained dimers of these dienes as impurities that could not be removed by distillation. The relative amounts of o- and m-isomers formed were determined in accordance with the following scheme:



a $R{=}CH_3$; $i{-}C_3H_7$

b $R{=}t{-}C_4H_9$

Hydrolysis of the adducts (XI) and (XII) permitted the separation of the dimers, and the resulting mixture of acids (XIII) and (XIV) was converted as in the preceding cases (dehydrogenation and nitric acid oxidation) either into a mixture of benzenedicarboxylic acids ($R = CH_3$, $i{-}C_3H_7$), or into a mixture of t-butylbenzoic acids ($R = t{-}C_4H_9$).

The results on the relative amounts of the structural isomers formed are given in the table for all the condensations studied.

This table shows that with increase in the size of the alkyl substituent, whether in the diene or in the dienophile, the structural selectivity of the reaction diminishes and the relative amount of the m-isomer in the mixture of adducts increases appreciably. We have shown previously [6] that in the condensations of 2-alkyl-1,3-butadienes the reverse relation is found: with increase in the size of substituents the relative amount of m-adduct diminishes, i.e., there is an increase in structural selectivity. Comparison of the results obtained for 1- and 2-substituted dienes enables us to draw some conclusions concerning the possible causes of this relation. If such changes in structural orientation in the series investigated by us depended solely on the electronic effects of the alkyl substituents, then the relative amounts of structural isomers would change in the same direction for 1-alkyl- as for 2-alkyl-1,3-butadienes, because the difference in electronic effects of the alkyl substituents must have the same sign irrespective of the position of the substituent (1- or 2-) in the diene. However, in actual fact the changes in structural orientation are directly opposite for 1- and 2-substituted dienes, which enables us to conclude that in the given case the electronic effects of substituents cannot play a determining part.

The results can apparently be explained by increase in the steric repulsion of substituent groups with increase in their size. It is clear that in this case there should be an increase in the relative amount of the adduct formed via the transition complex that is less hindered sterically. Examination of molecular models shows that in the case of 1-alkyl-1,3-butadienes m-isomers will be formed via the less hindered complexes, but in the case of 2-alkyl-1,4-butadienes it is the p-isomers that will be formed. This gives us reason to suppose that changes in the relative amounts of structural isomers as we pass from one alkylbutadiene to another are due mainly to steric factors (steric repulsion of substituents in the reaction) and that this hypothesis gives the most unequivocal explanation of the facts that we have established.

EXPERIMENTAL

trans-Piperylene (b.p. 41.5-42°, $n^{20}D$ 1.4295) was prepared by the isomerization of commercial piperylene with iodine [2]. 5-Methyl-1,3-hexadiene (b.p. 90-91°, $n^{20}D$ 1.4358) was prepared by the dehydration of 2-methyl-3-hexanol at 320° over zirconium dioxide deposited on pumice [7]. The hydrolysis of the adducts was carried out by boiling them for one hour with 50-100% excess of 10% methanolic NaOH [5]. Dehydrogenation was carried out in a flow system by repeated passage of the substance over palladized charcoal at 340-350° (size of layer 6 × 100 mm) until a constant refractive index was reached. Oxidation with dilute (10-15%) nitric acid was carried out by the procedure described in a previous paper [2]. As inhibitor in the diene condensations we used hydroquinone in an amount of 0.1-0.2% on the combined weight of diene and dienophile. Phthalic acid (m.p. 190-191°), dimethyl isophthalate (m.p. 64-65°), and also o- and m-t-butylbenzoic acids, were identified by mixture melting points with known samples.

Synthesis of 1,3-Octadiene. 2-Octen-3-ol (250 g; b.p. 80-82° (25 mm); $n^{20}D$ 1.4415 [8]) was dehydrated at 290-300° over zirconia on pumice (20% ZrO_2) (rate of feed 0.5 ml/min; size of catalyst layer 18 × 200 mm). We obtained 100 g (46.5%) of a mixture of dehydration products, b.p. 80-140°. Fractionation of this mixture through a column of 39-plate efficiency gave 15.0 g of 1,3-octadiene; b.p. 113-114° (751 mm); $n^{20}D$ 1.4350; λ_{max} 226 mμ; ϵ 27350 (in heptane). Found: 87.12, 87.07, H 12.70, 12.81%. C_8H_{14}. Calculated: C 87.21, H 12.79%.

We isolated also 8.3 g of a diene [b.p. 124-125° (751 mm); $n^{20}D$ 1.4273; λ_{max} 226 mμ; ϵ 12500 (in heptane)] which was not investigated further and 52 g of 2,4-octadiene; b.p. 132-132.5° (751 mm); $n^{20}D$ 1.4565; λ_{max} 228 mμ; ϵ 2400 (in heptane). The literature [8] gives: b.p. 132-134°; $n^{20}D$ 1.4545.

By oxidation of 1,3-octadiene with alkaline potassium permanganate by the method described earlier [6] we obtained a 48% yield of valeric acid, the p-bromophenacyl ester of which (m.p. 75-76°) showed no depression of melting point in admixture with a known sample.

Synthesis of 5,5-Dimethyl 1,3-hexadiene. A mixture of 120 g of 1-chloro-5,5-dimethyl-2-hexene (b.p. 50-60° (14 mm); $n^{15}D$ 1.4482 [9]), 600 ml of glacial acetic acid, and 300 g of fused potassium acetate was boiled for four hours. The hot mixture was poured into 1500 ml of water, the organic layer was separated, and the aqueous part was extracted twice with ether. The extract was dried over fused calcium chloride, ether was distilled off, and the residue was vacuum-distilled. This gave 113 g (81%) of 1-acetoxy-4-t-butyl-2-butene; b.p. 85-87° (17 mm); $n^{20}D$ 1.4322. Found: C 70.70; 70.62; H 10.59; 10.67%. $C_{10}H_{18}O_2$. Calculated: C 70.56; H 10.60%.

The resulting acetic ester (200 g) was passed in a stream of nitrogen at 510-520° through a catalysis tube (18 × 200 mm) filled with pieces of glass at the rate of 1 ml/min. The catalyzate was washed with water, with 5% sodium carbonate solution, and again with water; it was dried over fused calcium chloride. Vacuum fractionation gave 82 g (63%) of 5,5-dimethyl-1,3-hexadiene, b.p. 62-65° (170 mm). After fractionation through the 39-plate column the diene had: b.p. 106.5-106.8° (756 mm); $n^{20}D$ 1.1442; λ_{max} 225 mμ; ϵ 21000 (in heptane).

According to the literature [4] this diene has b.p. 106-107° (760 mm). Its adduct with maleic anhydride has m.p. 137-138°. The literature [4] gives m.p. 137-138°.

Condensation of Piperylene with Methyl Acrylate. 1) A mixture of 30 g of piperylene and 40 g of methyl acrylate was heated in a steel ampule at 200° for two hours. Vacuum fractionation gave 58 g (85%) of a mixture of the adducts (I) and (II) ($R = CH_3$); b.p. 94-97° (30 mm); $n^{20}D$ 1.4580. The literature [2] gives: b.p. 69-70° (6 mm); $n^{20}D$ 1.4588. The mixture of adducts (30 g) was dehydrogenated over palladized charcoal (20% Pd) at 340-350°. This gave 24 g (82%) of a mixture of the esters (III) and (IV) ($R = CH_3$), the hydrolysis of which gave 19.4 g (89%) of a liquid mixture of toluic acids. Oxidation of this with 140 ml of 15% nitric acid [2] gave 19 g (80%) of a mixture of benzenedicarboxylic acids, which was resolved by selective extraction with hot water into 14.9 g of phthalic acid and 2.2 g of isophthalic acid (ratio of 6.8 : 1).

2) A mixture of 34 g of piperylene and 43 g of methyl acrylate was kept in a sealed glass tube at room temperature (20°) for one year. Unchanged diene and dienophile were vacuum-distilled off at room temperature. Fractionation of the residue gave 49 g (64%) of a mixture of the adducts (I) and (II) ($R = CH_3$); b.p. 91-94° (25 mm); $n^{18}D$ 1.4580. The ratio of the amounts of o- and m-adducts, determined as in the preceding experiment, was 18 : 1.

3) A mixture of 68 g of piperylene and 172 g of methyl acrylate was passed at a rate of 2 ml/min at 400° through a Pyrex tube (20 × 600 mm) filled with pieces of glass and heated in an electric furnace. Vacuum fractionation gave 44 g (14%) of a mixture of the adducts (I) and (II) ($R = CH_3$); b.p. 92-95° (25 mm); $n^{21}D$ 1.4576. The ratio of the amounts of o- and m-adducts, determined as in the preceding experiments, was 3.7 : 1.

Condensation of 5-Methyl-1,3-hexadiene with Methyl Acrylate. A mixture of 15 g of 5-methyl-1,3-hexadiene and 15 g of methyl acrylate was heated in a steel ampule at 200° for five hours. Vacuum fractionation gave 17 g (60%) of a mixture of the adducts (I) and (II) ($R = i\text{-}C_3H_7$); b.p. 99-101° (10 mm); $n^{20}D$ 1.4633. Found: C 72.54; 72.65, H 9.92, 9.98%. $C_{11}H_{18}O_2$. Calculated: C 72.49, H 9.96%.

The mixture of adducts (23 g) was dehydrogenated over palladized charcoal (15% Pd) at 350-360°. This gave 18.7 g (83%) of the dehydrogenation products (III) and (IV) ($R = i\text{-}C_3H_7$), the hydrolysis of which with methanolic sodium hydroxide gave 12.8 g (74%) of a mixture of isopropylbenzoic acids. Oxidation of this with 350 ml of 10% nitric acid gave 9.5 g (73%) of a mixture of benzenedicarboxylic acids. Resolution of this mixture by selective extraction with hot water gave 7.6 g of phthalic acid and 1.5 g of isophthalic acid (ratio of 5 : 1).

Condensation of 1,3-Octadiene with Methyl Acrylate. A mixture of 10 g of 1,3-octadiene and 13 g of methyl acrylate was heated in a steel ampule at 200° for five hours. Vacuum fractionation of the reaction products gave 13.2 g (74%) of a mixture of the adducts (I) and (II) ($R = C_4H_9$); b.p. 143-146° (40 mm); $n^{20}D$ 1.4660. Found C 73.34, 73.50, H 10.21, 10.30%. $C_{12}H_{20}O_2$. Calculated: C 73.44, H 10.24%.

The adducts (12.5 g) were dehydrogenated over palladized charcoal (15% Pd) at 350-360°. This gave 9.9 g (81%) of a mixture of the esters (III) and (IV) ($R = C_4H_9$), hydrolysis of which with methanolic sodium hydroxide gave 7.1 g (78%) of a liquid mixture of butylbenzoic acids. Oxidation of this with 150 ml of 15% nitric acid gave 5.3 g (80%) of benzenedicarboxylic acids, separation of which by selective extraction with hot water gave 4.1 g of phthalic acid and 0.8 g of isophthalic acid (ratio of 5.1 : 1).

Condensation of 5,5-Dimethyl-1,3-hexadiene with Methyl Acrylate. A mixture of 12 g of 5,5-dimethyl-1,3-hexadiene and 12 g of methyl acrylate was heated in a steel ampule at 200° for five hours. Vacuum fractionation gave 16.3 g (76%) of a mixture of the adducts (I) and (II) ($R = t\text{-}C_4H_9$); b.p. 122-125° (20 mm); $n^{20}D$ 1.4665. Found: C 73.26, 73.21, H 10.15, 10.31%. $C_{12}H_{20}O_2$. Calculated: C 73.44, H 10.24%.

The mixture of adducts (21 g) was dehydrogenated over palladized charcoal (15% Pd) at 340-350°. This gave 18.1 g (88%) of dehydrogenation products, hydrolysis of which with methanolic sodium hydroxide gave 13.2 g (79%) of a mixture of t-butylbenzoic acids. Crystallization from acetone and petroleum ether gave 9.4 g of o-t-butylbenzoic acid, m.p. 68-69°, and 2.3 g of m-t-butylbenzoic acid, m.p. 127-128° (ratio of 4.1 : 1).

Condensation of piperylene with methyl methacrylate. A mixture of 30 g of piperylene and 45 g of methyl methacrylate was heated in a steel ampule at 200° for two hours. Vacuum fractionation gave 50 g (68%) of the mixture of adducts (VII) and (VIII) (R = CH_3); b.p. 88-91° (15 mm); $n^{20}D$ 1.4630. Hydrolysis of 42 g of the adducts gave 34 g (89%) of a liquid mixture of the acids (IX) and (X) (R = CH_3), b.p. 163-165° (40 mm). Decarboxylation and dehydrogenation of this mixture over palladized charcoal (20% Pd) at 340-350° gave 18.9 g (81%) of xylenes, the oxidation of which with 330 ml of 15% nitric acid gave 24.8 g (84%) of a mixture of benzenedicarboxylic acids. Extraction with hot water gave 18.5 g of phthalic acid, and the residue yielded 3.8 g of isophthalic acid (ratio of 4.9 : 1).

Condensation of 5-Methyl-1,3-hexadiene with Methyl Methacrylate. A mixture of 15 g of 5-methyl-1,3-hexadiene and 17 g of methyl methacrylate was heated in a steel ampule at 200° for five hours. Vacuum fractionation gave 15.9 g (52%) of a mixture of the adducts (VII) and (VIII) (R = i-C_3H_7); b.p. 113-117° (20 mm); $n^{20}D$ 1.4642. Hydrolysis of 22 g of the adducts with 10% methanolic sodium hydroxide gave 18.2 g (89%) of a liquid mixture of the acids (IX) and (X) (R = i-C_3H_7). Found: C 72.49, 72.59, H 9.90, 9.88%. $C_{11}H_{18}O_2$. Calculated: C 72.49, H 9.96%.

From 17 g of this mixture of acids, after decarboxylation and dehydrogenation over palladized charcoal (15% Pd) at 350-360°, we obtained 10.3 g (82%) of dehydrogenation products, the oxidation of which with 15% nitric acid gave 9.3 g (73%) of a mixture of benzenedicarboxylic acids. By separation of these by selective extraction with hot water we isolated 6.6 g of phthalic acid and 2.1 g of isophthalic acid (ratio of 3.1 : 1).

Condensation of 5,5-Dimethyl-1,3-hexadiene with Methyl Methacrylate. A mixture of 12 g of 5,5-dimethyl-1,3-hexadiene and 14 g of methyl methacrylate was heated in a steel ampule at 200° for five hours. Vacuum fractionation gave 17 g (75%) of a mixture of the adducts (VII) and (VIII) (R = t-C_4H_9); b.p. 132-135° (25 mm); $n^{20}D$ 1.4735. On hydrolysis of 19 g of the adducts with methanolic sodium hydroxide we isolated 15.3 g (86%) of a mixture of the acids (IX) and (X) (R = t-C_4H_9). Found: C 73.48, 73.46, H 10.07, 10.12%. $C_{12}H_{20}O_2$. Calculated: C 73.44, H 10.24%.

The mixture of acids (14 g) was decarboxylated and dehydrogenated over palladized charcoal (15% Pd) at 340-350°, and we obtained 8.2 g (77%) of dehydrogenation products, the oxidation of which with 100 ml of 10% nitric acid gave 8 g (81%) of a mixture of t-butylbenzoic acids. Crystallization of this mixture from acetone and petroleum ether gave 5.1 g of o-t-butylbenzoic acid, m.p. 68-69°, and 2.0 g of m-t-butylbenzoic acid, m.p. 128-129° (ratio of 2.6 : 1).

Condensation of Piperylene with Ethyl 2-Isopropylacrylate. A mixture of 20 g of piperylene and 42 g of ethyl 2-isopropylacrylate was heated in a steel ampule at 200° for 15 hr. Vacuum fractionation gave 20.4 g (33%) of a mixture of the adducts (XI) and (XII) (R = CH_3); b.p. 102-105° (8 mm); $n^{20}D$ 1.4670. Found: C 73.97, 73.94, H 10.34, 10.39%. $C_{13}H_{22}O_2$. Calculated: C 74.22, H 10.47%.

The mixture of the adducts (40 g) was hydrolyzed by boiling it for 25 hr with a 100% excess of 20% ethanolic sodium hydroxide. This gave 31 g (89%) of a mixture of the acids (XIII) and (XIV) (R = CH_3), which, without being distilled, was decarboxylated and dehydrogenated over palladized charcoal (20% Pd) at 340-350°. We isolated 18.5 g (81%) of a mixture of o- and m-cymenes. Oxidation of 12 g of this mixture with 260 ml of 15% nitric acid gave 12.4 g (83%) of benzenedicarboxylic acids. Separation of these by selective extraction with hot water gave 8.4 g of phthalic acid and 3.4 g of isophthalic acid (ratio of 2.5 : 1).

Condensation of 5-Methyl-1,3-hexadiene with Ethyl 2-Isopropylacrylate. A mixture of 10 g of 5-methyl-1,3-hexadiene and 17 g of ethyl 2-isopropylacrylate was heated in a steel ampule at 200° for ten hours. Vacuum fractionation gave 10 g of a mixture of the adducts (XI) and (XII) (R = i-C_3H_7) together with some 5-methyl-1,3-hexadiene dimer; b.p. 118-124° (10 mm); $n^{20}D$ 1.4682. Hydrolysis of 26 g of this mixture by boiling it with 20% ethanolic potassium hydroxide for 25 hr gave 5.2 g of unhydrolyzed material of b.p. 125-130° (25 mm); this was 5-methyl 1,3-hexadiene dimer. Found: C 87.16, 87.21, H 12.37, 12.31%. $C_{14}H_{24}$. Calculated: C 87.42, H 12.58%. We obtained also 14.7 g (88% on the amount of substance hydrolyzed) of a mixture of the acids (XIII) and (XIV) (R = i-C_3H_7).* Found: C 74.34, 74.30, H 10.53, 10.62%. $C_{13}H_{22}O_2$. Calculated: C 74.26, H 10.51%.

The mixture of acids (14 g) was decarboxylated and dehydrogenated over palladized charcoal (15% Pd) at 340-350°. We obtained 8.1 g (76%) of a mixture of o- and m-diisopropylbenzenes. Oxidation of 6 g of this

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*When account was taken of the amount of dimer isolated, the yield of adducts in the condensation was 32%.

mixture with 300 ml of 15% nitric acid gave 5.1 g (83%) of benzenedicarboxylic acids, from which we isolated 3.4 g of phthalic acid and 1.4 g of isophthalic acid (ratio of 2.4 : 1).

Condensation of 5,5-Dimethyl-1,3-hexadiene with Ethyl 2-Isopropylacrylate. A mixture of 23 g of 5,5-dimethyl-1,3-hexadiene and 36 g of ethyl 2-isopropylacrylate was heated in a steel ampule at 200° for 10 hr. Vacuum fractionation gave 13.2 g of a mixture of the adducts (XI) and (XII) (R = t-C_4H_9) and of the dimer of 5,5-dimethyl-1,3-hexadiene; b.p. 135-140° (25 mm); $n^{20}D$ 1.4680. The resulting mixture (18 g) was hydrolyzed by boiling it for 25 hr with excess of 20% ethanolic potassium hydroxide. This gave 4.3 g of 5,5-dimethyl-1,3-hexadiene dimer, b.p. 139-143° (25 mm), and 10.1 g (83% on the amount of substance hydrolyzed) of a mixture of the acids (XIII) and (XIV) (R = t-C_4H_9).* Found: C 74.92, 75.04, H 10.83, 10.84%. $C_{14}H_{24}O_2$. Calculated: C 74.98, H 10.75%.

The mixture of acids (XIII) and (XIV) (R = t-C_4H_9) (9.5 g) was decarboxylated and dehydrogenated over palladized charcoal (15% Pd) at 340-350°. The resulting dehydrogenation products (5.9 g, 79%) were oxidized with 150 ml of 10% nitric acid. This gave 4.9 g (81%) of a mixture of t-butylbenzoic acids, crystallization of which from acetone and petroleum ether gave 2 g of o-t-butylbenzoic acid, m.p. 68-69°, and 2.2 g of m-t-butylbenzoic acid, m.p. 128-129° (ratio of 0.9 : 1).

SUMMARY

1. Condensations were carried out between the 1-alkyl-1,3-butadienes (piperylene, 5-methyl-1,3-hexadiene, 1,3-octadiene, and 5,5-dimethyl-1,3-hexadiene) and acrylic, methacrylic, and 2-isopropylacrylic esters, and the relative amounts of the structural isomers formed were determined.

2. The relative amount of the m-isomer in the mixture of adducts increases with increase in the sizes of the alkyl substituents in the diene and dienophile, which finds its explanation in increased steric hindrance to the formation of the o-isomer.

3. In the case of the condensation of piperylene with methyl acrylate it was shown that with rise in temperature the content of m-isomer in the mixture of adducts increases.

LITERATURE CITED

1. R. L. Frank, R. D. Emmick, and R. S. Johnson, J. Am. Chem. Soc. 69, 2313 (1947).
2. I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, Zhur. Obshch. Khim. 25, 88 (1955).**
3. A. A. Petrov and N. P. Sopov, Zhur. Obshch. Khim. 27, 1795 (1957).**
4. K. Alder, K. Heimbach, and E. Kühle, Ber. 86, 1364 (1953).
5. I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1412 (1959).**
6. I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1595 (1959).**
7. I. N. Nazarov and M. V. Mavrov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 365 (1958).**
8. K. I. Karasev and A. V. Khabarova, Zhur. Obshch. Khim. 10, 1641 (1940).
9. A. A. Petrov and K. V. Lééts, Zhur. Obshch. Khim. 26, 1113 (1956).**

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*When account was taken of the amount of dimer isolated, the yield of adducts in the condensation was 19%.

**Original Russian pagination. See C. B. translation.