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Abstract

Full Text

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ON THE INTERACTION OF AZODICARBOXYLIC ESTER WITH gem-DIALKYLBUTADIENES

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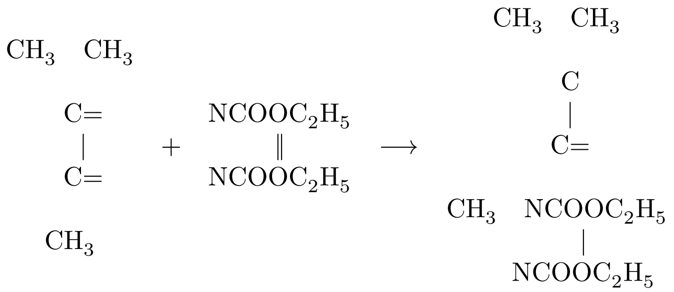
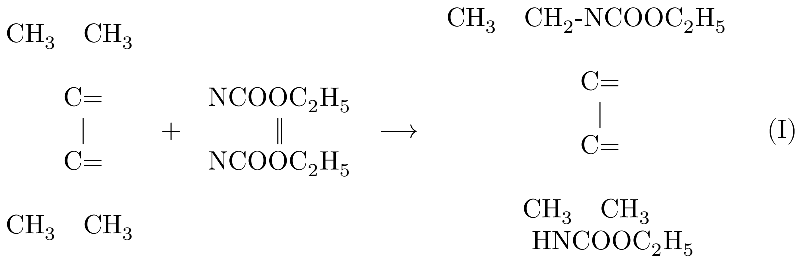
Continuing the investigation of the decomposition of alkyltetrahydropyridazines (^{1}), we attempted to synthesize gem-dialkyltetrahydropyridazines from adducts of azodicarboxylic ester with gem-dialkylbutadienes.

The interaction of azodicarboxylic ester with dienes of this structure was described by Diels et al. (^{2}) and later by us (^{3}). As gem-dialkylbutadienes, 2,4-dimethylpentadiene-1,3 (^{2,3}), 2-methylhexadiene-2,4 (^{3}), and 2,5-dimethylhexadiene-2,4 (^{3}) were used. The addition products were assigned the structure of 1,2-dicarbethoxy-Δ^4-tetrahydropyridazines, i.e., it was believed that in this case the reaction proceeds according to the usual scheme of diene synthesis:

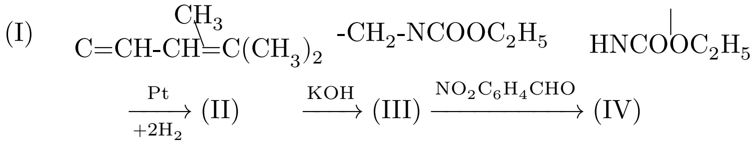


In the present work it is shown that the adducts of azodicarboxylic ester with gem-dialkylbutadienes in fact have not a cyclic structure (they are not derivatives of tetrahydropyridazines), but are monosubstituted hydrazodicarboxylic esters; i.e., the interaction of gem-dialkylbutadienes with azodicarboxylic ester proceeds not by the type of diene synthesis, but by the type of substituting addition. Thus, for example, 2,4-dimethylpentadiene reacts with azodicarboxylic ester in the following manner:



$$\begin{array}{c} CH_3 \quad CH_3 \\ C= \\ | \\ C= \\ CH_3 \quad CH_3 \end{array} + \begin{array}{c} NCOOC_2H_5 \\ \| \\ NCOOC_2H_5 \end{array} \longrightarrow \begin{array}{c} CH_3 \quad CH_2\text{-}NCOOC_2H_5 \\ C= \\ | \\ C= \\ CH_3 \quad CH_3 \\ HNCOOC_2H_5 \end{array} \quad (I)$$

The structure of the obtained adduct I was established on the basis of the study of some of its transformations. On hydrogenation in the cold it adds 2 moles of hydrogen per 1 mole of adduct and, thus, contains two double bonds in the molecule. Hydrolysis of adduct I leads not to 3,3,6,6-tetramethyl-Δ^4-tetrahydropyridazine (as should have been the case if addition had occurred by the type of diene synthesis), but to a monosubstituted hydrazine III. The presence of an NH_2 group in the latter was established by obtaining from it the benzylidene derivative IV:

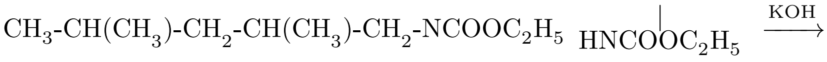


$$(I) \quad \overset{CH_3}{C=CH\text{-}CH=C(CH_3)_2}\text{-}CH_2\text{-}NCOOC_2H_5 \quad HNCOOC_2H_5$$
$$\xrightarrow[+2H_2]{Pt} (II) \quad \xrightarrow{KOH} (III) \xrightarrow{NO_2C_6H_4CHO} (IV)$$

When azodicarboxylic ester reacts with 2,4-dimethylpentadiene-1,3, which contains two kinds of methyl groups, two addition products, Va and Vb, may be formed (in fact, apparently, a mixture of these compounds is obtained). However, after hydrogenation both are converted into one and the same substituted hydrazodicarboxylic ester VI:

$$\text{2,4-dimethylpentadiene-1,3} + NCOOC_2H_5{=}NCOOC_2H_5$$
$$\longrightarrow (Va) \xrightarrow{+2H_2} (VI)$$
$$\longrightarrow (Vb) \xrightarrow{+2H_2} (VI)$$

The latter, upon hydrolysis, forms the monosubstituted hydrazine VII, which gives the benzylidene derivative VIII and, in addition, under the action of mercuric oxide evolves nitrogen and is converted into 2,4-dimethylpentane (this reaction is typical of monoalkylhydrazines (^{4})):



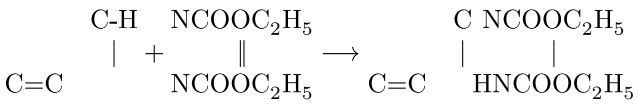
$$CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}NCOOC_2H_5 \quad HNCOOC_2H_5 \xrightarrow{KOH}$$

$$\text{KOH} \longrightarrow \underset{\text{(VII)}}{CH_3CH(CH_2CH(CH_3)_2)CH_2NHNH_2} \xrightarrow{NO_2C_6H_4CHO} \underset{\text{(VIII)}}{CH_3CH(CH_2CH(CH_3)_2)CH_2NHN{=}CHC_6H_4NO_2}$$

$$\xrightarrow{HgO,\ -N_2} (CH_3)_2CHCH_2CH(CH_3)_2$$

The reactions presented quite definitely indicate the acyclic structure of the addition products of gem-dialkylbutadienes to azodicarboxylic ester. Evidently, the dienes studied by us react with azodicarboxylic ester through one of their methyl groups.

The ability of azodicarboxylic ester to react with monoolefins by the type of substitutive addition has been described in the literature (5–8). It was shown that the reaction proceeds at the carbon atom located in the α-position with respect to the double bond (6):



$$\begin{array}{ccccccc} & \text{C-H} & & NCOOC_2H_5 & & \text{C} & NCOOC_2H_5 \\ & | & + & \| & \longrightarrow & | & | \\ C{=}C & & & NCOOC_2H_5 & C{=}C & & HNCOOC_2H_5 \end{array}$$

The substitutive addition of olefins to maleic anhydride, which has been studied in much greater detail, also occurs in the α-position (8). However, whereas maleic anhydride reacts in a similar manner only at 200–250°, in the case of the much more active azodicarboxylic ester the reaction already takes place at 20–50°.

Thus, in the present work it has been established for the first time that 1,1-dialkylbutadienes react with azodicarboxylic ester not through their double bonds, but through the labile hydrogen in the α-position (by the type of substitutive addition).

Experimental Part

Adducts of gem-dialkylbutadienes with azodicarboxylic ester. To a solution of 0.2 mole of diene (2,4-dimethylpentadiene-1,3 or 2,5-dimethylhexadiene-2,4) in 50 ml of anhydrous benzene, 35 g of azodicarboxylic ester is added (warming occurs during this), and the mixture is left for 5-7 hr at room temperature. The benzene is then distilled off, and the residue is distilled in vacuum in a stream of nitrogen. The adduct of 2,4-dimethylpentadiene-1,3 (V) is apparently a mixture of two isomeric heptadienylhydrazodicarboxylic esters: yield 70-75%; b.p. 172–175°/10 mm; n_D^{20}1.4760; d_4^{20}1.0637; MR 71.68, for $C_{13}H_{22}O_4N_2F_2$ calculated* 71.77.

Found % :	C	57.54;	57.37;	H 8.33;	8.15
$C_{13}H_{22}O_4N_2$. Calculated % :	C	57.74;		H 8.21	

Literature data (2): b.p. 136°/0.4–0.5 mm.

Adduct of 2,5-dimethylpentadiene-2,4 (I; 2,5-dimethylhexadien-2,4-yl-1-hydrazodicarboxylic ester): b.p. 185–187°/15 mm; n_D^{20}1.4738; d_4^{20}1.0390; MR_D 76.90, for $C_{14}H_{24}O_4N_2F_2$ calculated 76.39.

Found % : C 59.01; 58.98; H 8.50; 8.37
$C_{14}H_{24}O_4N_2$. Calculated % : C 59.13; H 8.51

Hydrogenation of the adducts. Hydrogenation of the adducts is carried out cold (in a "duck") in abs. alcohol (40% solution) in the presence of plati- of fresh catalyst. Over 8–12 h, 1.85–1.95 mol of hydrogen is absorbed per 1 mol of adduct. The catalyst is separated by centrifugation, the alcohol is distilled off, and the residue is distilled in vacuo under nitrogen.

2,4-Dimethylpentyl-1-hydrazodicarboxylate (VI; from the adduct of 2,4-dimethylpentadiene-1,3): yield 92%; b.p. 169–170°/10 mm; n_D^{20} 1.4530; d_4^{20} 1.0207; MR_D 72.64, calculated for $C_{13}H_{26}O_4N_2$: 72.70.

Found, %: C 56.90; 56.82; H 9.50; 9.44
$C_{13}H_{26}O_4N_2$. Calculated, %: C 56.91; H 9.55

2,5-Dimethylhexyl-1-hydrazodicarboxylate (II; from the adduct of 2,5-dimethylhexadiene-2,4): yield 90%; b.p. 175–176°/8 mm; n_D^{20} 1.4570; d_4^{20} 1.0120; MR_D 77.61, calculated for $C_{14}H_{28}O_4N_2$: 77.32.

Found, %: C 58.41; 58.45; H 9.50; 9.44
$C_{14}H_{28}O_4N_2$. Calculated, %: C 58.31; H 9.56

Hydrolysis of hydrazodicarboxylates. Hydrolysis was carried out on the adduct of 2,5-dimethylhexadiene with azodicarboxylate ester (I) and on the hydrogenated adduct of 2,4-dimethylpentadiene-1,3 (VI).

To a solution of 0.1 mol of hydrazodicarboxylate in 50 ml of ethyl alcohol is added a solution of 29 g (0.5 mol) of caustic potash in 50 ml of alcohol, and the mixture is heated for 3–4 h on a water bath. The precipitated potassium salt is filtered off and washed with ether; the solvent is distilled from the filtrate, and the residue is distilled in vacuo under nitrogen.

2,5-Dimethylhexadien-2,4-yl-1-hydrazine (III; from the adduct of 2,5-dimethylhexadiene-2,4)—a viscous oil, distilling with decomposition and unstable in air: b.p. 88–90°/20 mm. The *p*-nitrobenzylidene derivative (IV): m.p. 303° (from acetic acid).

Found, %: C 66.00; 65.83; H 7.03; 6.88
$C_{15}H_{19}O_2N_3$. Calculated, %: C 65.91; H 7.01

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* Here and below, the atomic refraction of nitrogen was taken as equal to 2.48 (3).

2,4-Dimethylpentyl-1-hydrazine (VII; from the hydrogenated adduct of 2,4-dimethylpentadiene-1,3): b.p. 84–85°/25 mm; n_D^{20} 1.4550; d_4^{20} 0.8533; MR_D 41.40, calculated for $C_7H_{18}N_2$: 41.68.

Found, %: C 65.30; 65.36; H 12.60; 12.60; N 21.91; 21.87
$C_7H_{18}N_2$. Calculated, %: C 65.60; H 12.60; N 21.80

p-Nitrobenzylidene derivative (VIII): m.p. 112–113° (from acetic acid).

Found, %: C 63.70; 63.65; H 8.01; 7.87
$C_{14}H_{21}O_2N_3$. Calculated, %: C 63.85; H 8.04

Oxidation of 2,4-dimethylpentyl-1-hydrazine. To a solution of 13 g (0.1 mol) of 2,4-dimethylpentylhydrazine in 50 ml of ether, with vigorous stirring, 32.5 g (0.15 mol) of yellow mercuric oxide is gradually added. Heating and vigorous evolution of gas are observed (2.0 l; 98% N_2). After completion of the reaction, the ethereal solution is decanted from the precipitate of metallic mercury and excess mercuric oxide, dried with calcium chloride, the ether is distilled off with a high-efficiency dephlegmator, and the 2,4-dimethylpentane formed is isolated by distillation of the residue: yield 72%; b.p. 79–80°/752 mm; n_D^{20} 1.3830; d_4^{20} 0.6745. Literature data (^{9}): b.p. 80.7°/760 mm; n_D^{20} 1.3821; d_4^{20} 0.6738.

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named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.