Chemistry

Academician **I. N. Nazarov** and M. V. Mavrov

1958

SovietRxiv

Abstract

Full Text

Chemistry

Academician **I. N. Nazarov** and M. V. Mavrov

On Diene Condensations of gem-Substituted Butadienes

The question of the possibility of gem-substituted butadienes entering into diene synthesis has until recently remained open. Apart from certain works ($^{1-3}$) that have appeared recently, the diene condensations of these dienes were known only from patent data.

At the same time, a number of authors have noted that dienes of this type do not enter into the reaction at all (^{4}), or, as shown by the example of condensations with maleic anhydride, form only polymeric products.

We undertook a detailed investigation of such condensations. As the simplest gem-substituted dienes we selected 1,1-dimethyl- (I), 1,1,2-trimethyl- (II), 1,1,3-trimethyl- (III), 1,1,4-trimethyl- (IV), 1,1-dimethyl-2-isopropyl- (V)-butadienes and diisocrotyl (VI), the preparation of which, with the exception of 1,1,3-trimethylbutadiene (III), was specially developed by us; maleic anhydride, acrylonitrile, methyl acrylate, and crotonaldehyde were used as dienophiles (see Table 1).

Dienes I, IV, and VI with maleic anhydride under various conditions (temperature, time, solvent, etc.) gave only polymeric products, whereas 1,1,2-trimethyl- (II) and 1,1-dimethyl-2-isopropyl- (V)-butadienes with maleic anhydride (100°, 15 hr) formed adducts in yields of 40 and 70%, respectively.

On further investigation it proved that the compounds obtained correspond to adducts of the isomeric form of the starting dienes, i.e.

$$\text{gem-substituted butadiene} \longrightarrow \text{isomeric conjugated diene} + \text{maleic anhydride} \longrightarrow \text{cyclohexene anhydride a}$$

$$R = \mathrm{CH_3},\ \mathrm{CH(CH_3)_2}.$$

The use of dienophiles less reactive than maleic anhydride requires more severe temperature conditions (for diisocrotyl, for example, 230—260°); in this case condensation of dienes I, IV, and VI is accompanied by considerable formation of polymers, and the yields of condensation products amount to only 15–30%. Thus, we succeeded in bringing into the reaction all the dienes studied by us (see Table 1). The structure of the adducts obtained was proved by their dehydrogenation over a chromium oxide catalyst on alumina (in the presence of gem-dimethyl groups, dehydrogenation over it is accompanied only by demethanation) or by 20% palladium on charcoal and subsequent oxidation to the known aromatic acids.

On dehydrogenation of the acid obtained by saponification of the adduct of diisocrotyl VI with methyl acrylate, both over Cr_2O_3/Al_2O_3 and over Pd/C, and subsequent oxidation with dilute nitric acid under pressure, only isophthalic acid was isolated, and not terephthalic acid, which would correspond to the normal addition product. The course of the reactions described can be represented by the scheme:

diisocrotyl $\longrightarrow$ isomeric diene + $CH_2{=}CHCO_2CH_3$ $\longrightarrow$ methyl cyclohexenecarboxylate adduct $\longrightarrow$ cyclohe
$\longrightarrow$ cyclohexanecarboxylic acid $\longrightarrow$ substituted benzene $\longrightarrow$ isophthalic acid ($C_6H_4(CO_2H$

Similarly, the condensations of 1,1-dimethylbutadiene (I) proceed with complete preliminary isomerization of the diene. In proving the structure, we were able to show the presence of both structural isomers corresponding to 1,3-dimethylbutadiene, with a content of the meta isomer of about 5–7%.

[[reaction scheme: isomerization/condensation of 1,1-dimethylbutadiene with acrylonitrile, followed by transformations to cyano-, carboxy-, and tricarboxy-substituted aromatic products; substituent labels visible include CN, CO_2H, and HO_2C]]

Obviously, in the course of the reaction, migration of the double bonds occurs in the starting dienes according to the type of an allylic shift, with formation of 1,3-disubstituted butadienes. The occurrence of this type of isomerization was recently pointed out by Alder and Schumacher in their review (^{5}), which appeared during the course of the present work; however, the authors completely deny the possibility that gem-substituted dienes enter into diene synthesis without their preliminary isomerization. As we have been able to establish, in fact, some gem-substituted dienes directly enter into diene condensation; however, along with adducts of normal structure, products from isomeric forms of the starting diene are formed, which indicates partial isomerization of the dienes under the condensation conditions.

Thus, 1,1,4-trimethylbutadiene (IV) with methyl acrylate forms a mixture of isomeric esters containing about 60% of the normal adduct, as was found from the ratio of benzoic and terephthalic acids in the transformation products according to the scheme:

[[reaction scheme: 1,1,4-trimethylbutadiene and its isomeric form condense with methyl acrylate; subsequent transformations lead to cyclohexene carboxylates/acids and then to aromatic acids; visible substituent labels include CO_2CH_3 and CO_2H]]

The condensation product of 1,1,2-trimethylbutadiene (II) with methyl acrylate is a mixture of at least three adducts corresponding both to the normal form and to isomeric forms of diene II, the presence of which was established by the following series of transformations:

[[reaction scheme: three pathways for 1,1,2-trimethylbutadiene/isomeric dienes with methyl acrylate, followed by transformations through cyclohexene carboxylates/acids to substituted aromatic carboxylic acids; visible substituent labels include CO_2CH_3 and CO_2H]]

The benzoic, *o*-phthalic, and hemimellitic acids isolated in this way in a ratio of 1 : 2 : 5 approximately correspond to the content of isomeric esters in the initial mixture.

Upon oxidation with moist silver oxide of the mixture of aldehydes obtained in the condensation of 1,1,2-trimethylbutadiene (II) with crotonaldehyde, crystalline 2,2,3,6-tetramethyl-Δ^3-tetrahydrobenzoic acid was isolated in pure form (20–25% of the mixture of acids); its structure was proved by conversion into trimellitic acid. By dehydrogenating the remaining mixture of acids, followed by oxidation and separation, isophthalic, trimellitic, and prehnitic acids were isolated in approximately equal proportions. Thus, the content of the normal addition adduct in the mixture of aldehydes amounts to about 50%.

[Reaction scheme showing the condensation products from 1,1,2-trimethylbutadiene with crotonaldehyde, their oxidation/dehydrogenation, and conversion into benzoic, isophthalic, trimellitic, and prehnitic acid derivatives.]

The behavior of 1,1-dimethyl-2-isopropylbutadiene (V) was studied by us using its condensation with methyl acrylate as an example.

[Reaction scheme showing two condensation pathways of 1,1-dimethyl-2-isopropylbutadiene with methyl acrylate, followed by hydrolysis/oxidation and conversion into o*-phthalic and hemimellitic acids.]*

Upon dehydrogenation of the mixture of acids obtained by saponification of the adduct and subsequent oxidation, *o*-phthalic and hemimellitic acids were isolated in a ratio of 1 : 3, i.e., in this case as well partial formation of the normal addition product takes place.

An exception in this series of dienes is 1,1,3-trimethylbutadiene (III). The latter, as had already been known earlier, reacts with unusual ease with various dienophiles, forming normal adducts in good yields.

Upon dehydrogenation of the mixture of nitriles obtained by condensation of 1,1,3-trimethylbutadiene (III) with acrylonitrile, over Cr_2O_3/Al_2O_3, followed by saponification and oxidation according to the scheme:

[Reaction scheme showing condensation of 1,1,3-trimethylbutadiene with acrylonitrile to nitrile adducts, dehydrogenation to aromatic nitriles, hydrolysis to carboxylic acids, and oxidation to tricarboxylic acids.]

along with trimellitic acid, trimesic acid corresponding to the meta isomer was isolated; its content is about 3–5%.

Thus, it was established that 1,1-dimethylbutadiene and diisocrotyl enter into diene synthesis only after preliminary isomerization into 1,3-disubstituted dienes and do not form normal condensation adducts at all. 1,1,2-Trimethyl-, 1,1,4-trimethyl-, and 1,1-dimethyl-2-isopropylbu—

Table 1

Dienes	Methyl acrylate: reaction conditions, °C	Methyl acrylate: reaction conditions, h	Methyl acrylate: yield, %	Methyl acrylate: b.p., °C/mm Hg	Methyl acrylate: n_D^{20}	Acrylonitrile: reaction conditions, °C	Acrylonitrile: reaction conditions, h	Acrylonitrile: yield, %	Acrylonitrile: b.p., °C/mm Hg	Acrylonitrile: n_D^{20}	Crotonaldehyde: reaction conditions, °C	Crotonaldehyde: reaction conditions, h	Crotonaldehyde: yield, %	Crotonaldehyde: b.p., °C/mm Hg	Crotonaldehyde: n_D^{20}
structural formula as drawn: $CH_2 = C(CH_3) - CH = CH_2$	—	—	—	—	—	220	4	23	76–81/7	1.4708	150	14	18	85–90/16	1.4723
structural formula as drawn: $(CH_3)_2C = CH - CH = CH_2$	200	4	66	82–84/4	1.4701	200	5	72	98–101/7	1.4749	200	2	71	90–92/6	1.4778
structural formula as drawn: $(CH_3)_2C = C(CH_3) - CH = CH_2$	220	2	67	69–72/3	1.4651	200	2	75	67–68/3	1.4705	200	2	18	87–89/15	1.4804
structural formula as drawn: $(CH_3)_2C = CH - C(CH_3) = CH_2$	200	14	18	88–90/14	1.4535	—	—	—	—	—	220	8	12	70–80/6	1.4720

Dienes	Methyl acrylate: reaction conditions, °C	Methyl acrylate: reaction conditions, h	Methyl acrylate: yield, %	Methyl acrylate: b.p., °C/mm Hg	Methyl acrylate: n_D^{20}	Acrylonitrile: reaction conditions, °C	Acrylonitrile: reaction conditions, h	Acrylonitrile: yield, %	Acrylonitrile: b.p., °C/mm Hg	Acrylonitrile: n_D^{20}	Crotonaldehyde: reaction conditions, °C	Crotonaldehyde: reaction conditions, h	Crotonaldehyde: yield, %	Crotonaldehyde: b.p., °C/mm Hg	Crotonaldehyde: n_D^{20}
structural formula as drawn: $(CH_3)_2C=C(CH_3)-C(CH_3)=CH_2$	170	7	64	94–97/4	1.4692	200	5	60	129–131/15	1.4782	200	4.5	40	83–86/3	1.4795
structural formula as drawn: $(CH_3)_2C=CH-CH=C(CH_3)_2$	260	4	30	95–99/5	1.4662	—	—	—	—	—	230	5	15	85–88/4	1.4758

tadienes, along with adducts of the isomeric forms of the geminal diene, also form normal products of diene synthesis. And only 1,1,3-trimethylbutadiene enters normally into the diene-synthesis reaction.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
21 XII 1957

CITED LITERATURE

1. G. Dupont, R. Dulou, G. Christen, *Bull. Soc. Chim.*, 820 (1954).
2. H. Euler, H. Hasselquist, *Ark. Kemi*, **6**, 139 (1953).
3. Y.-R. Naves, P. Ardizio, *Helv. Chim. Acta*, **31**, 2252 (1948).
4. G. B. Bachmann, R. E. Hatton, *J. Am. Chem. Soc.*, **66**, 1513 (1944).
5. *Fortschritte der Chemie Organischer Naturstoffe*, Wien, **10**, 1953, pp. 1–118.