Chemistry

V. F. Kucherov, E. P. Serebryakov, and R. E. Valter

1961

SovietRxiv

Reaction scheme showing compounds (I)-(IX), with substituents CO_2CH_3(a), CO_2CH_3(e), CO_2H, CO_2R, NH_2, and transformations including CH_2N_2, CH_3ONa, H_2(Pt), H_3O^+, and HN_3.

Figure 1: Reaction scheme showing compounds (I)-(IX), with substituents CO_2CH_3(a), CO_2CH_3(e), CO_2H, CO_2R, NH_2, and transformations including CH_2N_2, CH_3ONa, H_2(Pt), H_3O^+, and HN_3.

Abstract

Full Text

Chemistry

V. F. Kucherov, E. P. Serebryakov, and R. E. Valter

Study of the Structural and Spatial Direction of the Diene Condensation of 1-Vinylcyclopentene with Methyl Acrylate

(Presented by Academician B. A. Kazanskii, February 4, 1961)

It is known (^{1}) that the condensation of 1-vinylcyclohexene with methyl acrylate gives predominantly geometric isomers of the ortho structure, which is consistent with the regularities of the structural direction of the diene synthesis of 1,2-disubstituted dienes with unsymmetrical dienophiles (^{2}).

We have shown that the condensation of 1-vinylcyclopentene with methyl acrylate proceeds less unambiguously, and that of the four theoretically possible isomers (I–IV), at least three are formed in comparable amounts. Interaction of the components at room temperature (30 days) or on boiling their solution in benzene (24 hours) leads to a mixture of methyl esters which cannot be separated by fractional distillation or adsorption chromatography. Alkaline saponification of this mixture gives a liquid mixture of acids, from which it is possible to isolate in pure form (yield $\sim 15\%$) only cis-Δ^7-hydrindene-5-carboxylic acid (V). Its structure and configuration were proved by conversion into the known cis-cis-hydrindane-5-carboxylic acid (VI) (^{3}) and further into the known cis-cis-5-aminohydrindane (VII) (^{4}). Pure meta-cis ester (III) is not capable of isomerization by sodium methoxide, which confirms the equatorial orientation of its carbomethoxy group. The double bond in the meta-cis acid (V) is readily displaced into the position between the rings already on boiling its aqueous solution in the presence of maleic acid. The Δ^8-hydrindene-5-carboxylic acid (VIII) formed in this process, upon catalytic hydrogenation, gives the cis-cis acid (VI).

Under conditions of migration of the double bond from the liquid mixture of acids remaining after separation of the meta-cis acid (V), it is possible to isolate a further ca. 15% of the Δ^8-acid (VIII) and a low-melting γ-lactone (IX). The formation of the latter indicates the presence in the original mixture of adducts

Fig. 1 chromatogram

Figure 2: Fig. 1 chromatogram

Fig. 2 chromatogram

Figure 3: Fig. 2 chromatogram

of the ortho-cis isomer (I); however, the impossibility of isolating this isomer in an individual state does not permit a sufficiently rigorous decision as to its relative content in the mixture of adducts.

Fig. 1. Chromatogram of a mixture of adducts of 1-vinylcyclopentene with methyl acrylate. *a* —initial mixture of esters; *b* —mixture of esters after isomerization with CH_3ONa; *c* —the same after addition of pure meta-cis ester (III)

Fig. 2. Chromatogram of the products of isomerization of the initial mixture of adducts with HCl in acetic acid. *a* —mixture of esters after isomerization with HCl and CH_3COOH; *b* —the same after addition of pure meta-ester (VIII, $R = CH_3$)

To determine the composition of the mixture of adducts of 1-vinylcyclopentene with methyl acrylate, we applied the method of gas–liquid chromatography. It turned out that this mixture consists of at least three isomers (ratio of peak areas 25 : 7 : 10), with peak 3 corresponding to the meta-cis isomer (III) (Fig. 1). The composition of the mixtures of adducts obtained at 20 and at 80° is practically identical; the substances tested undergo no changes upon passage through the column.

The initial mixture of adducts, on boiling with sodium methoxide (isomerization of axial carbomethoxy groups into equatorial ones) and treatment of the resulting mixture of acids with diazomethane, is converted into a mixture of only the structural isomers (II) and (III). The chromatogram of this mixture gives two peaks with an area ratio of 3 : 2. Since, as a result of alkaline isomerization, peak 2 disappears, peak 1 remains practically unchanged, and peak 3 (the meta-cis isomer III) increases, it is obvious that, in the initial mixture, peak 2 corresponds to the meta-trans isomer (IV), while peak 1 represents the ortho adduct (possibly in the form of a mixture of the cis and trans isomers I and II). The formation in comparable amounts (10 : 7) of both meta isomers (III and IV) gives grounds to believe that, in the case of meta orientation of the components of the diene synthesis, the principle of “maximum accumulation of unsaturation” does not play a special role.

Comparison of the sum of the areas of peaks 3 and 2 with the area of peak 1 in the chromatogram of the initial mixture of esters shows that the ratio of adducts of ortho and meta structure formed in the diene synthesis is approximately 3 : 2. For additional confirmation of this conclusion, the initial mixture of adducts was converted, by acid isomerization, into a mixture of ortho and meta isomers with the double bond located between the rings. Analysis of the mixture obtained shows the presence of two peaks with an area ratio of 3 : 2 (Fig. 2), with peak 2 identified as the ester of the meta acid (VIII, R = CH_3).

Thus, the ratio of structural isomers (ortho and meta) in all three cases is 3 : 2. Apparently, the peculiarity of the conform-

of 1-vinylcyclopentene reduces the directing role of the electronic factor, as a result of which the formation of a considerable amount of meta adducts is also observed in the diene synthesis.

Comparison of the results of chromatographic analysis with the amount of isolated acids of the meta series and γ-lactone (IX) shows that formation of this lactone is possible only from the ortho-cis adduct (I). However, it is impossible to estimate accurately the amount of this isomer in the mixture of adducts, since the low yield of γ-lactone (~15%) may be explained not only by the predominance of the ortho-trans isomer (II), but also by a possible shift of the double bond under the lactonization conditions, with formation of Δ^8-hydrindene-4-carboxylic acid.

Experimental Part

Isolation and proof of the structure of meta-cis acid (V). A mixture of 24 g of methyl acrylate, 20 g of 1-vinylcyclopentene [^5], 30 ml of dry benzene, and 0.1 g of pyrogallol was boiled for 24 hours; the solvent was distilled off and the liquid residue was distilled in vacuo. There was obtained 27.3 g of a mixture of adducts (yield 71.4%) with b.p. 135–136°/30 mm, n_D^{15} 1.4929. On standing of a benzene solution of the components at room temperature for a month, the same mixture of adducts was obtained in 48% yield.

25 g of the above mixture of adducts was boiled until complete dissolution with 120 ml of 10% aqueous caustic soda; the solution was filtered with activated charcoal and acidified with hydrochloric acid. The oil which separated was extracted with ether (3 × 50 ml), the extract was dried with sodium sulfate, and the solvent was distilled off. The resulting liquid mixture of acids partially crystallized on standing. After two crystallizations from a mixture of ether with petroleum ether, 3.36 g (14.6%) of pure meta-cis acid (V) was isolated, m.p. 125–126°.

Found, %:	C 72.04; 71.81; H 8.41; 8.43
$C_{10}H_{14}O_2$. Calculated, %:	C 72.26; H 8.49

Treatment of the latter with diazomethane gave pure meta-cis ester (III), b.p. 114–116°/13 mm, n_D^{20} 1.4913.

A solution of 1.7 g of meta-cis acid (V) in 20 ml of methanol was hydrogenated over platinum oxide, and 1.6 g of cis-cis-hydrindane-5-carboxylic acid (VI) was obtained. After two crystallizations from isopentane it melted at 50–52°, and the amide obtained from it has m.p. 194–195°, which corresponds to the literature data [^3]. On treating a solution of meta-cis acid (VI) in chloroform with sodium azide and sulfuric acid (40°, 1 hour), cis-cis-5-aminohydrindane (VII) was obtained; its benzamide has m.p. 141–143°, which corresponds to the literature data [^4].

Preparation of meta acid (VIII) and γ-lactone (IX). A mixture of 10 g of the liquid mixture of acids remaining after isolation of the meta-cis isomer (V), and 1.5 g of maleic acid in 250 ml of water was boiled for 4 hours, after which the reaction mixture was saturated with sodium bicarbonate and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and the solvent was distilled off. There was obtained 2.35 g of a liquid product, which was chromatographed twice on neutral alumina (activity grade IV, elution with benzene). 1.45 g of pure γ-lactone (IX) was isolated, with m.p. 21–22.5° and n_D^{25} 1.5028; in its IR spectrum there is an intense band at 1780 cm^{-1}.

Found, %:	C 72.10; 71.90;	H 8.41; 8.49
$C_{10}H_{14}O_2$. Calculated, %:	C 72.26;	H 8.49

The aqueous alkaline solution was acidified with hydrochloric acid and extracted with ether (3 × 50 ml). After drying the extract over sodium sulfate

and after removal of the solvent we obtained 1.25 g of meta acid (VIII), which after crystallization from petroleum ether melted at 105–106°.

$C_{10}H_{14}O_2$.	Found, %:	C 72.14; 72.05;	H 8.33; 8.56
	Calculated, %:	C 72.26;	H 8.49

The same acid was obtained in 78% yield by boiling an aqueous solution of the meta-cis acid (V) in the presence of maleic anhydride. On hydrogenation with a Pt catalyst it forms the meta-cis-cis acid (VI) described above, and on treatment with diazomethane—the corresponding ester (VIII, $R = CH_3$) with b.p. 115–118°/11 mm and n_D^{20} 1.4930.

Study of mixtures of esters by gas-liquid chromatography. Analysis of the mixtures was carried out on a simple apparatus (6) with a slightly modified microflame detector and with a column length of 1.5 m. Hydrogen served as the mobile phase (pressure 1.28 atm, flow rate 75 ml/min); as the stationary liquid phase, silicone oil with an addition of 6% lithium capronate, deposited on kieselguhr, was used. The optimum column temperature was 145–155°. Samples (0.02–0.03 ml) were introduced into the evaporator with a microsyringe. For the method of calculating peak areas, see (7).

a) The initial mixture of adducts, obtained by both methods described above, gave on analysis three peaks with an area ratio of 25 : 7 : 10 (2.54 : 0.73 : 1 and 2.50 : 0.68 : 1). The chromatogram of the mixture of esters obtained on saponification of the initial adduct followed by treatment of the mixture of acids with diazomethane has the same character.

b) To a solution of 6.3 g of sodium in 200 ml of absolute methanol, 9.5 g of the initial mixture of adducts was added; the mixture was boiled for 15 h and the solvent was removed by distillation. The residue was saponified by boiling with 100 ml of water, the aqueous solution was filtered with charcoal and acidified with hydrochloric acid. The separated oil was extracted with benzene (3 × 100 ml) and then with 100 ml of ether. The crystalline product remaining after removal of the solvents (m.p. 43-76°) was treated with diazomethane, giving 6.5 g of a mixture of esters (II) and (III) with b.p. 115-118°/14 mm. On analysis this mixture gave two peaks with an area ratio of 3 : 2 (1.55 : 1; 1.62 : 1 and 1.52 : 1).

c) 10 g of the initial mixture of adducts was heated for 1 h at 65-70° with a mixture of glacial acetic acid and acetic anhydride saturated with dry hydrogen chloride (15 ml). The solvents were removed in vacuum and the residue was heated for 6 h at 85-90° with 6 ml of pyridine. The solution was poured into 200 ml of water and extracted with benzene (3 × 50 ml); the benzene extract was washed with dilute hydrochloric acid, dried over magnesium sulfate, and the solvent was removed. We obtained 4.9 g of a mixture of ortho- and meta-Δ^8-esters with b.p. 115-118°/12 mm. On analysis this mixture gave two peaks with an area ratio of 3 : 2 (1.52 : 1 and 1.61 : 1).

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

Received
28 I 1961

CITED LITERATURE

1. I. N. Nazarov, V. F. Kucherov, G. M. Segal, *Izv. AN SSSR, OKhN*, 1956, 559.

2. I. N. Nazarov, A. I. Kuznetsova, N. V. Kuznetsov, *ZhOKh*, **25**, 88 (1955).

3. W. G. Dauben, J. Jiu, *J. Am. Chem. Soc.*, **76**, 4426 (1954).

4. W. Hückel, *Lieb. Ann.*, **533**, 1 (1937).

5. V. F. Kucherov, E. P. Serebryakov, *Izv. AN SSSR, OKhN*, 1960, 1057.

6. B. A. Rudenko, S. S. Yufit, L. N. Ivanova, V. F. Kucherov, *Izv. AN SSSR, OKhN*, 1960, 1147.

7. A. A. Zhukhovitskii, B. A. Kazanskii, O. D. Sterligov, N. M. Turkeltaub, *DAN*, **123**, No. 6, 1037 (1958).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.