CHEMISTRY

Academician A. N. NESMEYANOV, A. E. BORISOV, and N. V. NOVIKOVA

1958

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. N. NESMEYANOV, A. E. BORISOV, and N. V. NOVIKOVA

RETENTION OF THE CONFIGURATION OF THE PROPENYL RADICAL IN REACTIONS OF cis- AND trans-PROPENYLLITHIUM WITH OXO COMPOUNDS

In previous communications ([1]) we showed that reactions of electrophilic and homolytic exchange at the olefinic carbon atom responsible for cis-, trans-isomerism proceed with retention of the geometrical configuration.

This was demonstrated for numerous metal-for-metal exchanges. The aim of the present work was to investigate from the same point of view the electrophilic replacement of a metal atom by a carbon atom in reactions of cis- and trans-propenyllithium with oxo compounds.

The isomers of propenyllithium were obtained by the action of metallic lithium on the cis- and trans-isomers of propenyl bromide in dry ether. Both stereoisomers of propenyl bromide were synthesized by dehydrobromination of 1,2-dibromopropane ([2]), and after their separation by distillation on a column with an efficiency of 60 theoretical plates were immediately introduced into the reaction.

The trans-isomer had b.p. 62.5–63°, n_D^{16} 1.4561, while the cis-isomer boiled at 57° and had n_D^{16} 1.4570. Their configurations are known ([3]).

On investigation of the infrared absorption spectrum of a 15–20% ethereal solution of the stereoisomers of propenyllithium, it was found that propenyllithium obtained from cis-propenyl bromide has vibrational frequencies (in cm^{-1}): 700; 726; 736; 845; 890; 922; 1028–1185; 1285; 1350; 1390; 1450; 1480; 1562; 1623; 1852; 1874, while propenyllithium obtained from trans-propenyl bromide has vibrational frequencies (in cm^{-1}): 736; 845; 890; 922; 975; 1022–1170; 1285; 1302; 1350; 1388; 1450; 1484; 1645; 1960. The characteristic vibrational frequencies for cis-compounds of this type are 700 and 1623 cm^{-1}, and for their trans-isomers 975 and 1645 cm^{-1}. On the basis of these data, propenyllithium obtained from cis-propenyl bromide must be regarded as a cis-compound, and propenyllithium prepared from trans-propenyl bromide as a trans-compound.

To an ethereal solution of cis- or trans-propenyllithium there was added, respectively, an equivalent amount (calculated for 0.008 mole) of a ketone or aldehyde in 200 ml of dry ether*. After two hours' stirring and decomposition with a sat-

urated solution of ammonium chloride, the reaction product dried with potash was subjected to distillation.

We investigated the products of the reactions of cis- and trans-propenyllithium with acetone, acetophenone, benzophenone, *p*-chlorobenzophenone, and also with acetaldehyde and benzaldehyde.

In each case, from cis-propenyllithium with ketones we obtained the corresponding tertiary, and with aldehydes secondary, alcohols possessing the cis-configuration, while trans-propenyllithium reacted with the same reagents to form the corresponding trans-compounds.

* For all experiments propenyllithium was prepared from 10 g (0.008 mole) of propenyl bromide and 1.10 g (0.016 mole) of metallic lithium in dry ether at 5-7°.

Table 1

Vibrational frequencies of the IR absorption spectra of the reaction products of stereoisomeric propenyllithium with aldehydes and ketones (in cm^{-1})

Compound	Isomer	Frequencies, cm^{-1}
$CH_3CH{=}CH{-}C(CH_3)_2OH$	cis-	640; 660; 700; 770; 790; 900; 1080; 1140; 1280; 1356; 1660
$CH_3CH{=}CH{-}C(CH_3)_2OH$	trans-	660; 770; 790; 900; 970; 1090; 1140; 1280; 1370; 1670; 1680
$CH_3CH{=}CH{-}C(OH)(C_6H_5)(CH_3)$	cis-	700; 764; 850; 924; 960; 1090; 1124; 1150; 1260; 1370; 1600; 1680; 1900; 1960
$CH_3CH{=}CH{-}C(OH)(C_6H_5)(CH_3)$	trans-	764; 800; 880; 920; 970; 1070; 1124; 1150; 1290; 1370; 1450; 1604; 1680; 1810; 1890; 1960
$CH_3CH{=}CH{-}C(C_6H_5)_2OH$	cis-	610; 670; 700; 740; 850; 924; 990; 1160; 1260; 1300; 1450; 1650
$CH_3CH{=}CH{-}C(C_6H_5)_2OH$	trans-	610; 650; 700; 770; 850; 974; 996; 1160; 1260; 1320; 1360; 1450; 1654
$CH_3CH{=}CH{-}C(OH)(C_6H_4Cl)(C_6H_5)$	cis-	610; 660; 700; 760; 840; 930; 1000; 1090; 1130; 1190; 1220; 1320; 1400; 1450; 1660

Compound	Isomer	Frequencies, cm^{-1}
$CH_3CH{=}CH{-}C(OH)(C_6H_4Cl)(C_6H_5)$	trans-	610; 630; 700; 764; 836; 914; 980; 996; 1090; 1190; 1280; 1320; 1380; 1400; 1450; 1660
$CH_3CH{=}CH{-}CH(OH)(CH_3)$	cis-	733; 848; 910; 945; 1019; 1063; 1102; 1135; 1300; 1378; 1400; 1438; 1655; 2900
$CH_3CH{=}CH{-}CH(OH)(CH_3)$	trans-	860; 910; 960; 1022; 1059; 1110; 1147; 1300; 1364; 1398; 1437; 1675; 2900
$CH_3CH{=}CH{-}CH(OH)(C_6H_5)$	cis-	702; (720–740); 759; 864; 909; (970–986); 1031; 1074; 1106; 1174; 1227; 1379; 1440; 1442; 1449; 1593; 1655; 2900
$CH_3CH{=}CH{-}CH(OH)(C_6H_5)$	trans-	702; 759; 845; 913; 960; 1004; 1064; 1115; 1191; 1225; 1372; 1440; 1487; 1592; 1661; 2900
$CH_3CH{=}CH{-}CH(CH_3)OC_6H_4NO_2$	cis-	721; 746; 790; 834; 850; 876; 890; 1012; 1030; 1104; 1161; 1273; 1347; 1529; 1596; 1722
$CH_3CH{=}CH{-}CH(CH_3)OC_6H_4NO_2$	trans-	719; 792; 836; 874; 899; 965; 1013; 1042; 1108; 1124; 1163; 1288; 1359; 1532; 1600; 1720

Table 2

Physicochemical constants of the reaction products of propenyllithium stereoisomers with aldehydes and ketones

Starting substances: formula $CH_3CH{=}CHLi$	Starting substances: aldehyde and ketone	Reaction temp., °C	Reaction products	b.p., °C	Pressure, mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	m.p. of n-nitrobenzoate, °C	Yield, %
cis-	CH_3COCH_3	−2	$CH_3\backslash C{=}C(/C(CH_3)_2OH)$	60–61	72	1.4352	0.8435	31.00	30.97	53–54.5	51
trans-	CH_3COCH_3	0	$CH_3\backslash C{=}C(/H)/C(CH_3)_2OH$	65–67	72	1.4328	0.8356	31.14	30.97	65–66	54
cis-	$CH_3COC_6H_5$	−5	$CH_3\backslash C{=}C(/C(C_6H_5)(CH_3)OH)$	80–81	3	1.5310	0.9934	50.52	50.51		68
trans-	$CH_3COC_6H_5$	−2	$CH_3\backslash C{=}C(/H)/C(C_6H_5)(CH_3)OH$	86	4	1.5329	0.9961	50.53	50.51		67
cis-	$C_6H_5COC_6H_5$	0	$CH_3\backslash C{=}C(/C(C_6H_5)_2OH)$	145	3	1.5901**	1.0757**	70.38	69.94		66
trans-	$C_6H_5COC_6H_5$	−2	$CH_3\backslash C{=}C(/H)/C(C_6H_5)_2OH$	152–154*	3	1.5860**	1.0704**	70.31	69.94		68.4
cis-	n-$ClC_6H_4COC_6H_5$	0	$CH_3\backslash C{=}C(/C(C_6H_5)(C_6H_4Cl)OH)$	165	2	1.6011	1.1774	75.28	74.81		63
trans-	n-$ClC_6H_4COC_6H_5$	0	$CH_3\backslash C{=}C(/H)/C(C_6H_5)(C_6H_4Cl)OH$	160–162	3	1.5963	1.1708	75.21	74.81		62
cis-	CH_3CHO	0	$CH_3\backslash C{=}C(/CH(CH_3)OH)$	65.5	70	1.4315	0.8476	26.28	26.35	77.5–78	52
trans-	CH_3CHO	0	$CH_3\backslash C{=}C(/H)/CH(CH_3)OH$	64–65	74	1.4281	0.8371	26.48	26.35	54–55	58
cis-	C_6H_5CHO	−5	$CH_3\backslash C{=}C(/CH(C_6H_5)OH)$	101–102	6	1.5400	1.0109	45.98	45.84	56–57	58
trans-	C_6H_5CHO	−5	$CH_3\backslash C{=}C(/H)/CH(C_6H_5)OH$	102	5	1.5370	1.0039	46.10	45.84	98–99	56
	$CH_3C{\equiv}C-\underset{OH}{\overset{H}{C}}-CH_3$	20	$CH_3\backslash CH{=}CH/CH(CH_3)OH$	63–65	70	1.4311	0.8472	26.27	26.35	77–78	37

* Freezing point, 20.5°.

** Constants obtained for 25°.

The assignment of the configurations of the reaction products was made on the basis of the vibrational frequencies of the IR absorption spectra, summarized in Table 1*.

The characteristic vibrational frequencies for trans compounds are the region 960–980 cm^{-1}—the out-of-plane C—H vibration—and the region of frequencies

of the C–C double-bond vibration, which is higher in trans compounds than in cis compounds.

In addition to the vibrational frequencies in the region of the C–C bond, cis compounds are characterized by the presence of a vibrational frequency in the region of 700 cm^{-1} and the complete absence of a vibrational frequency at 960-980 cm^{-1}.

It should be noted that exactly the same frequencies of the IR spectrum are possessed by the reaction products that were not subjected to purification by distillation.

We made use of the well-known fact of the catalytic addition of two hydrogen atoms to acetylene derivatives in the cis position ([4]) and separately synthesized the cis isomer of 1-methylbuten-2-ol-1 by partial hydrogenation of methylpropenylcarbinol in the presence of Raney nickel, thereby additionally confirming its configuration.

The cis and trans isomers of 1,1-dimethylbuten-2-ol-1, 1-methylbuten-2-ol-1, and 1-phenylbuten-2-ol-1 were also identified in the form of the *p*-nitrobenzoates (see Table 2).

Thus, the reactions of cis- and trans-isomeric organometallic derivatives of olefins with the metal at the olefinic carbon in reactions with oxo compounds (just as we have also shown for the carbonation reaction by means of CO_2) ([5]) preserve the configuration of the olefinic radical.

The rule we have established for the retention of the configuration of the olefinic radical in electrophilic and homolytic substitution at the olefinic carbon has, as was to be expected, general significance.

Received
20 XI 1957

CITED LITERATURE

1. a) A. N. Nesmeyanov, A. E. Borisov, DAN, **60**, No. 1, 67 (1948); b) A. N. Nesmeyanov, A. E. Borisov, A. N. Abramova, Izv. AN SSSR, OKhN, **1946**, 647; **1947**, 289; **1948**, 570; c) A. N. Nesmeyanov, A. E. Borisov, V. D. Vil' chevskaya, Izv. AN SSSR, OKhN, **1954**, 1008; d) A. N. Nesmeyanov, A. E. Borisov, N. A. Vol' kenau, Izv. AN SSSR, OKhN, **1954**, 992; **1956**, 162.

2. J. Wislicenus, H. Sandbein, Lieb. Ann., **243**, 325 (1888); M. G. Chavann, M. Ch. Mouren, C. R., **156**, 1700 (1914).

3. N. B. Hannay, Ch. P. Smith, J. Am. Chem. Soc., **68**, 1005 (1946); M. G. Rogers, J. Am. Chem. Soc., **69**, 1243 (1947); K. S. Harwell, L. F. Hatch,

J. Am. Chem. Soc., **77**, 1682 (1955).

4. K. Campbell, B. Campbell, Chem. Rev., **31**, 145 (1942).

5. A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova, DAN, **96**, No. 2, 289 (1954).

---

* The IR absorption spectra of the first four cis-trans isomers (see Table 1) were made at our request by L. A. Kazitsyna and G. A. Rudenko (Moscow State University), and those of the remaining three stereoisomers by V. N. Smorchkov (Optical Laboratory of the Institute of Organoelement Compounds, Academy of Sciences of the USSR), to whom we express our gratitude.

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