CHEMISTRY

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

1958

SovietRxiv

scheme of transformations of cis- and trans-propenyl organometallic compounds, with numbered reaction arrows 1-25 and X = Cl and Br

Figure 1: scheme of transformations of cis- and trans-propenyl organometallic compounds, with numbered reaction arrows 1-25 and X = Cl and Br

Abstract

Full Text

CHEMISTRY

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

PRESERVATION OF THE CONFIGURATION OF THE PROPENYL RADICAL IN REACTIONS OF TRANSITION FROM METAL TO METAL

Continuing our investigations (1) on the stereochemistry of exchange reactions of atoms bonded to olefinic carbon, we carried out the series of transformations of the cis- and, correspondingly, trans-propenyl radical, summarized in Table 1, starting from stereoisomeric 1-bromo-1-propenes. These bromides were converted by the action of lithium in ether at a temperature from +5 to −7° into the corresponding stereoisomeric propenyllithiums and then, by successive exchanges at lowered temperatures, into a series of propenyl organometallic compounds of Hg, Sn, Tl, and, by the action of CO_2, into the corresponding stereoisomers of crotonic acid.

The configuration of the starting bromopropenes (2), as well as of crotonic and isocrotonic acids, is known. The configuration of both propenyllithiums,

Table 1

obtained by the action of lithium on an ethereal solution of the corresponding bromopropene at 5—7°, was proved by us by the presence, in the IR spectrum of the substance formed from cis-bromopropene, of frequencies 700 and 1623 cm^{-1}, and in the IR spectrum of its stereoisomer of frequencies 975 and 1645 cm^{-1}*, which characterizes the first organolithium substance as the cis- and the second as the trans-isomer.

The exchange reactions of both isomers of propenyllithium with $HgBr_2$ and $TlBr_3$ proceeded with retention of configuration, as did all the other metal

---

* The IR absorption spectra of the stereoisomers of propenyllithium were made at our request by L. A. Kazitsyna and G. A. Rudenko, for which we express our gratitude to them.

exchanges studied by us. This is proved by the separation of the region of transformations of *cis*-propenyllithium from the region of transformations of the *trans*-lithium compound and by the method of even and odd cycles [1]. Indeed, the transitions 6, 7; 7, 8; 5; 7, 8, 12, 11, 5; 7, 8, 12, 11, 9, 6 and 11, 9, 10 in the series of transformations of *trans*-propenyllithium, and the corresponding transformations 18, 19; 19, 20, 17; 19, 20, 24, 17; 23, 24; 23, 21, 22, include 2, 3, 5, 6 links; they are cyclic, i.e., each time they return to the initial stereoisomer, irrespective of the number of links in the cycle. Therefore any possibility of reactions with inversion of configuration is excluded.

Thus, the material presented in this article (partly already reported [3]) again confirms the rule established by us concerning retention of configuration in electrophilic or homolytic substitutions at olefinic carbon.

In the present work the transformations 1, 13, 8, 20, 11 and 23 are evidently homolytic; the others are electrophilic. All reactions were carried out at temperatures below room temperature. For precisely this reason we could not use the reaction $R_2TlX + Hg \rightarrow R_2Hg$, which we had previously employed—it requires a considerably higher temperature.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
20 XI 1957

CITED LITERATURE

[1] a) A. N. Nesmeyanov, A. E. Borisov, *DAN*, **60**, 1, 67 (1948); b) A. N. Nesmeyanov, A. E. Borisov, A. N. Abramova, *Izv. AN SSSR, OKhN*, 1946, 674; 1947, 289; 1949, 570. A. N. Nesmeyanov, A. E. Borisov, V. D. Vilichevskaya, *Izv. AN SSSR, OKhN*, 1954, 1008; c) A. N. Nesmeyanov, A. E. Borisov, N. A. Volkenau, *Izv. AN SSSR, OKhN*, 1954, 992; 1956, 162.
[2] N. B. Hannay, Ch. P. Smith, *J. Am. Chem. Soc.*, **68**, 1005 (1946); M. T. Kogers, *J. Am. Chem. Soc.*, **69**, 1243 (1947); K. E. Harwell, L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).
[3] A. N. Nesmeyanov, A. E. Borisov, *Tetrahedron*, **1**, No. 1/2, 157 (1957).

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