REACTION OF ALLENE CYCLODIMERS WITH ALKYLLITHIUM COMPOUNDS

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The process of thermodimerization of an allene-methylacetylene fraction from the pyrolysis of petroleum products has recently been developed [1, 2], the main products of which are cyclic dimers of allene, 1,2- (I) and 1,3-dimethylenecyclobutane (II), and also a codimer of allene with methylacetylene, 1-methyl-3-methylenecyclobutane (III).



In the present work, we studied the reactions of (I)-(III) with alkyllithium compounds. The reactions of these types of compounds with nucleophilic reagents virtually have not been investigated previously. In [3] mention has been made of the easy isomerization of (II) into (III) in the presence of alkali metal alcoholates. The authors of [4] report an unsuccesful attempt to polymerize (III) under the influence of alkyllithium compounds, while 3-methylene-cyclobutene with a structure similar to that of (III) preferentially forms polymers containing 1,2-units under these conditions. In [5] organolithium compounds (IV) and (V) were obtained by the action of butyllithium on 1,2-dimethyl-3,4-dimethylenecyclobutene and 1,2,3-trimethyl-4-methylenecyclobutene, which contain a π -electronic system delocalized on five carbon atoms. Pentadienyl complexes of this type are known for alkali metals (for example



(VI)), and for alkaline earth and transition metals [6]. Pentadienyl complexes of alkali metals are usually obtained by the reaction of linear 1,4-dienes (but not 1,3-dienes) with alkyllithium compounds in polar media (THF) or with Na or K amides in liquid NH_3 , and also by metallation of 1,3- and 1,4-dienes by the action of alkali metals in the presence of tertiary amines [6].

We found that in the presence of THF at ~20°C, compounds (II) and (III) practically instantly react with ethyllithium, with a quantitative liberation of ethane. This indicates a metallation reaction, similar to that described in [5]. The reaction of (II) (a 1,4diene) with RLi (R = Et, i-Pr, sec-Bu) also proceeds slowly at ~20°C in hydrocarbon solvent medium (benzene, toluene), while (III) does not react under these conditions. In a THF medium both (II) and (III) are readily metallated at -20°C with a quantitative yield of ethane in the course of 1 h. Comparison with the data on pentadienyl complexes of lithium obtained from linear dienes [6] shows that the presence of a strained four-membered ring markedly increases the activity of the diene in the metallation reaction.

The structure of metallation products (II) and (III) was studied by spectral methods. The reaction was carried out in THF in an excess of diene to obtain a complete conversion of alkyllithium. The volatile products were then distilled off, the precipitate was washed with cold pentane and dried in vacuo. According to IR and PMR spectral data (see below) it was found that during the metallation of (II) and (III) one and the same complex is formed, which contains several THF molecules.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1996-1999, September, 1988. Original article submitted March 30, 1987. In the PMR spectrum of a complex obtained by reaction of (II) or (III) with isopropyllithium-d₇ in THF-d₈, signals at 2.39, 2.45, 2.58 and 3.92 ppm (2:2:2:1) are observed. The weakfield signal at 3.92 ppm corresponds to the H^D proton at the ring C³ atom (the resonance from its analogous proton in complex (VI) has a chemical shift of 4.1 ppm [7]), while the remaining signals correspond to the ring methylene group H^d protons and exocyclic methylene group protons (H^a, H^c, and H^a and H^c) at C¹ and C⁵. The signals of the terminal methylene protons of the pentadienyl system in complex (IV) are also in the form of two singlets at 2.46 and 2.27 ppm, while in complex (V) they appear in the form of a singlet at 2.3 ppm [5]. In general, the observed PMR spectrum of the metallation product (II) and (III) corresponds to the structure of (VII).



No information is available in the literature on the vibrational spectra of pentadienyl complexes. It was found that the IR spectra of complex (VII) have much in common with the spectra of the comprehensively investigated π -alkenyl systems. In the spectra of solutions of (VII) in THF or THF-d₈, broad intense absorption bands are observed for the Li-C bond at 590-610 cm⁻¹, and bands indicating the presence of a delocalized π -electronic system: at 500 cm⁻¹ (deformational vibrations of the (C-C-C) angles, 970, 1160, and 1250 cm⁻¹ (mixed vibrations of the carbon skeleton and of the C-C-H angles in the π -alkenyl group), and also at 1545 cm⁻¹ (v.s.) (the C=C stretching vibrations) [8]. Thus, the IR spectrum of the metallation product (II) and (III) does not contradict the proposed structure of (VII).

The metallation of (II) and (III) can be represented by the following scheme:

(II) $\xrightarrow{\text{LiR}}$ $\xrightarrow{\text{LiR}, \text{THF}}$ (III)

 (\mathbf{M})

In the first case, the metallation proceeds at the methylene group of the cyclobutane ring (II), and in the second, the methyl group of (III) is metallated.

Complex (VII) is very stable both in solid state, and in the form of a solution in THF and in an inert atmosphere (argon). When it is decomposed by water in a hydrocarbon medium, compound (III) is formed (GLC, PMR), while decomposition in THF gives a mixture of (III) and (II) in a 9:1 ratio, irrespective of the diene from which complex (VII) was obtained. The preferential formation of (III) during the hydrolysis of (VII) is probably due to its higher thermodynamic stability. Metallation of (II) and (III) by alkyllithium compounds, followed by treatment of complex (VII) by alkyl or silyl halides is used as a convenient method of functionalization of unsaturated derivatives of cyclobutane. At the same time, complex (VII) does not react with conjugated dienes: at 20-50°C it does not cause polymerization of (I), butadiene and isoprene.

In contrast with (II) and (III), the conjugated diene (I) is not metallated by alkyllithium compounds, but adds them, and in the presence of an excess of diene its polymerizes [9]. The reaction of equimolar amounts of (I) and isopropyllithium-d₇ was studied by the PMR method. In the spectrum of the product obtained in toluene-d₈, equal intensity singlets are observed at 0.5; 1.83; 2.34 and 2.44 ppm. The high field signal at 0.5 ppm corresponds to H^a protons and indicates a localization of the charge at C¹. The signal with 1.83 ppm corresponds to methylene protons H^d, while the signals with 2.44 and 2.34 ppm should be assigned, respectively, to H^b and H^c protons of the cyclobutane ring in (VIII). Decomposition of (VIII) with water leads to the formation of product (IX), in whose spectrum the signals should be assigned as follows: 1.57 (3H^a), 1.83 (2H^d), 2.31 ppm (4H^b,^c).



In the spectrum of the adduct of (I) with isopropyllithium-d₇ obtained in THF-d₈, compared with the spectrum in toluene, a small high-field shift is observed of signals of the H^b and H^c protons (2.39 and 2.22 ppm) and a more appreciable low-field shift of H^a (0.86 ppm) and H^d (2.00 ppm) proton signals, which is clearly a result of a charge redistribution from C¹ to C³ due to complexation with THF. Complex (VIII) models the terminal group of a growing polymeric chain during anionic polymerization of (I), and therefore we can state that its structure is not basically different from the structures of terminal units postulated in the polymerization of linear dienes [10].

In the IR spectrum of the product of the reaction of (I) with sec-BuLi in benzene, intense bands are observed in the 485-565 cm⁻¹ region, corresponding to the stretching vibrations of the Li-C bonds. The set of bands (cm⁻¹): 1540 w (vC=C), 1465 v.s, 1380 s, 1140 m, 1070 m, 1020 w, 970 s, 800 m, 680 m (δ C-C-H, δ H-C-H, vC-C) characterizes the delocalized structure (of the π -alkenyl type) of the ligand bound to the Li atom. The presence of the 1140 and 1070 cm⁻¹ bands can serve as an indication of an anti-configuration of the ligand [8]. The high intensity of the 1380 and 1465 cm⁻¹ bands is probably due to the presence of a terminal sec-Bu group. The band at 1680 cm⁻¹, characterizing the C=C bond of the 1,4-unit of a polymer of (I) is absent in the spectrum, but there is an intense band at 1610 cm⁻¹. This band can be assigned to the stretching vibrations of the C=C bond of the cyclobutene ring, coordinated with the metal. It is possible that in the system there is certain amount of a product of a consecutive addition of two molecules of (I) at the Li-C(X) bond. The band at 1610 cm⁻¹ is most sensitive to the oxidation of the sample in air. Even after 30 sec, its intensity sharply decreases, and in the spectrum a band at 1680 cm⁻¹ appears, characteristic of the C=C bond in the 1,4-polymer of (I).



(X)

EXPERIMENTAL

A mixture of allene thermodimers was obtained from the All-Union Scientific Research Institute of Organic Synthesis. Compounds (I)-(III) were isolated from this mixture and had a \geq 98% purity. Their PMR spectra correspond to the data in [4, 11].

The synthesis and investigation of complexes (VII) and (VIII) were carried out in an atmosphere of dry argon, purified from traces of oxygen. The samples for recording the IR spectra were prepared in a container in a dry inert atmosphere. The spectra were measured in hermetic cuvettes on a UR-20 spectrophotometer in the 400-4000 cm⁻¹ region. The PMR spectra of complexes (VII) and (VIII) were recorded at 36°C on Varian-60 (in THF-d₈) and Bruker HX-270 (in THF-d₈ and toluene-d₈ at a concentration of 0.3-0.5 mole/liter) spectrometers. The values of the chemical shifts of the resonance signals in the spectra are given with reference to tetramethylsilane.

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CONCLUSIONS

1,3-Dimethylenecyclobutane and 1-methyl-3-methylenecyclobutene are metallated in the presence of THF by alkyllithium compounds under mild conditions with the formation of one and the same organolithium compound of the π -pentadienyl type. Under the same conditions, 1,2-dimethylenecyclobutane adds alkyllithium compounds, to form a π -alkenyl complex.

LITERATURE CITED

- 1. S. P. Chernykh, A. I. Rudenkov, I. V. Kalechits, et al., Khim. Promst., No. 6, 335 (1982).
- S. P. Chernykh, A. M. Taber, A. I. Rudenkov, et al., Neftepererab. Neftekhim., No. 7, 48 (1981).
- F. F. Caserio, S. H. Perker, R. Pissolini, and J. D. Roberts, J. Am. Chem. Soc., <u>80</u>, 5507 (1958).
- 4. C. C. Wu and R. W. Lenz, J. Polym. Sci., Polym. Chem. Ed., <u>10</u>, 3259 (1972).
- 5. D. Seebach and B. Graf, Angew. Chem., 80, 532 (1968).
- 6. H. Yasuda and A. Nakamura, J. Organomet. Chem., <u>285</u>, 15 (1985).
- 7. R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, Tetrahedron Lett., 205 (1967).
- 8. G. N. Bondarenko and A. V. Kotov, Dokl. Akad. Nauk SSSR, 235, 840 (1977).
- 9. A. V. Yurkovetskii, V. L. Kofman, and K. L. Makovetskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1993 (1988).
- 10. W. H. Glaze, I. E. Hanicak, M. L. Moore, and I. Chaudhuri, J. Organomet. Chem., <u>44</u>, 39 (1972).
- 11. P. D. Bartlett, A. S. Wingrove, and R. Owyang, J. Am. Chem. Soc., <u>90</u>, 6067 (1968).