Experimental

Potentiometric measurements, hydrogenation, ¹H NMR measurements, and determination of the enantiomeric composition of phenylalanine produced upon hydrogenation were performed as described in Ref.⁵ All N-acetyldehydrodipeptides were prepared from the respective azlactones.⁶

References

1. D. Bacciola, E. Balestreli, R. A. Felicioli, A. Fissi, and O. Pieroni, *Chim. Ind.* (*Milan*) 1976, **58**, 519.

- 2. H. B. Kagan, Bull. Soc. Chim. Fr., 1988, 5, 846.
- 3. K. Tanimura, M. Waki, S. Lee, Ya. Kodera, and N. Izumiya, Bull. Chem. Soc. Jpn, 1984, 57, 2193.
- 4. I. N. Lisichkina, A. I. Vinogradova, B. O. Tserevitinov, M. B. Saporovskaya, V. K. Latov, and V. M. Belikov, *Tetrahe-dron: Asymmetry*, 1990, 1, 567.
- I. N. Lisichkina, A. I. Vinogradova, N. B. Sukhorukova, M. B. Saporovskaya, and V. M. Belikov, *Izv. Akad. Nauk. Ser. Khim.*, 1992, 1667 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1992, **42**, 1293 (Engl. Transl.)].
- 6. J. P. Greenstein and M. Winitz, Chemistry of the Amino Acids, Wiley, New York, 1961.

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Improved method for the synthesis of pentaphenylcyclopentadiene

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An improved method for the synthesis of pentaphenylcyclopentadiene is suggested. It involves the reaction of tetraphenylcyclopentadienone with PhMgBr and subsequent treatment of the reaction mixture with an excess of LiAlH_4 in THF. The effect of arylating agents and reducing agents on the yield of the target product is studied. The method suggested can be used for synthesizing other polyaromatic cyclopentadienes, in particular, 1,2,5-triphenyl-3,4-(1,8-naphthylene)cyclopentadiene.

Key words: pentaphenylcyclopentadiene, polyaromatic cyclopentadienes, synthesis.

Substituted cyclopentadienes are undoubtedly very common ligands in transition-metal chemistry. Recent trends show increased use of pentaphenylcyclopentadiene $(C_5 Ph_5 H)$, whose complexes with d elements are promising catalysts in stereo- and regioselective organic syntheses.¹⁻⁴ Syntheses of C₅Ph₅H which involve the addition of PhM to tetraphenylcyclopentadienone (cyclone) followed by isolation of the respective alcohol, its conversion into the bromide, and reduction of the latter by BuLi or Zn/H⁺ have been described.¹⁻³ A promising method,⁴ which makes it possible to prepare the target product in two stages in high yield, is based on the direct conversion of the alcohol into C₅Ph₅H under the combined action of LiAlH₄ and AlCl₃. With the availability of cyclone in mind,^{5,6} we focused on the development of a one-step one-pot synthesis of C_5Ph_5H .

Results and Discussions

Previously, a reaction of carbonyl compounds with Grignard-like ytterbium reagents of the PhYbI type was found,⁶⁻⁹ leading to formation of hydrocarbons through addition and deoxygenation stages. Unfortunately, an attempt to obtain C_5Ph_5H directly from cyclone failed: when the reaction was carried out in THF, a mixture containing a small amount of C_5HPh_4OH , C_5Ph_5H , and some unidentified compounds was obtained. We suppose that the low chemoselectivity of the reaction is caused by the tendency of reagents of the PhYbI type not only for 1,2-addition at the carbonyl group, but also for side reactions, such as the reduction of the double bond conjugated with the aromatic ring.¹⁰

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N₂	PhM	Reducing agent	Time (h)	Solvent	Yield (%)
1	PhLi	Ph ₂ Li	7	THF-C ₆ H ₁₄	75
2	PhLi	LiAlH ₄	7	THF-C ₆ H ₁₄	80
3	PhLi	LiAlH ₄	3	Et ₂ O	33
4	PhLi	LiAlH ₄	3	THF-Et ₂ O	84
5	PhLi	LiAlH ₄	3	Et ₂ O-C ₆ H ₁₄	34
6	PhMgBr	LiAlH ₄	3	Et ₂ O	36
7	PhMgBr	LiAlH ₄	1	THF-Et ₂ O	53
8	PhMgBr	LiAlH ₄	0,15	THF	97
9	PhMgBr	NaH	1	THF	0
10	PhMgBr/CeCl ₃	NaH	1	THF	0
11	PhMgBr	NaBH ₄	1	THF	0
12	PhLi/CeCl ₃	LiAlH ₄	1,5	THF-C ₆ H ₁₄	86
13	PhMgBr/CeCl ₃	LiAlH ₄	0.1	THF	95

Table 1. Synthesis of pentaphenylcyclopentadiene

Note. The yields were determined by HPLC with $C_{10}H_8$ as the standard.

A change in the nature of the organometallic compound and use of an additional reducing agent with their simultaneous introduction into the reaction mixture make it possible to prepare C_5Ph_5H without isolation of intermediates. We used PhLi and PhMgX with and without CeCl₃ as the phenyl-group donors and Ph₂Li, LiAlH₄, NaH, and NaBH₄ as reducing agents.



 $M = Li, MgBr, Li/CeCl_3, MgBr/CeCl_3$

The results obtained are summarized in Table 1. They demonstrate that C_5Ph_5H is formed in a nearly quantitative yield from cyclone with PhMgBr-LiAlH₄ in THF (entry 8), as well in the presence of CeCl₃ (entry 13).¹¹ The use of Ph₂Li as the reducing agent decreases the yield and results in contamination of the target product with biphenyl (entry 1). The use of PhLi has no advantage over PhMgBr for the preparation of C_5Ph_5H (entries 2–5). Reducing agents such as NaH, NaH/CeCl₃, and NaBH₄ do not react with the resulting alcoholate (entries 9, 11).

We studied the reactivity of the cyclone analogs, phencyclone and acecyclone * under the conditions found. The reaction with acecyclone leads to the quantitative formation of the desired 1,2,5-triphenyl-3,4-(1,8naphthylene)cyclopentadiene. Its structure was reliably established by mass spectrometry, ¹H NMR, and data from elemental analysis. In contrast, phencyclone reacts nonselectively to give no less than five compounds, among which the target cyclopentadiene (δ 5.15 (s, 1 H, C-H)) and the respective alcohol (δ 2.52 (s, 1 H, OH))¹² were identified by ¹H NMR spectroscopy and HPLC.

This method is not applicable to benzophenone and fluorenone, since the alcoholates obtained in the first stage cannot be reduced.

Thus, the method suggested is a handy route for synthesizing pentaphenylcyclopentadiene and its analogs.

Experimental

All solvents and starting reagents were purified by known procedures. Cyclone, phencyclone, and acccyclone were prepared as described, ¹³ their mps were 218, 273, and 289°C respectively, which correspond to the literature data.⁵ NMR spectra were recorded on a Varian VXR-400 spectrometer. Mass spectra were recorded on a Finigan MAT-113 mass spectrometer. The product yields were determined by HLPC on a Gilson chromatograph with a UV-VIS detector ($\lambda = 254$ nm) and the GME-714 program on a column packed with Silasorb C18 and with 96 % aqueous methanol as the eluent at a flow rate of 1.1 mLmin⁻¹.

Synthesis of Ar_5C_5H . General procedure. The corresponding cyclone (150 mmol) was added in one portion to a solution of PhMgBr (225 mmol) in THF at 20–30°C. The mixture was stirred for 10–15 min, and then LiAlH₄ (750 mmol) was added portionwise over 10–15 min. The mixture was stirred for additional 10–15 min, and then quenched with a saturated aqueous solution of NH₄Cl. The reaction products were extracted with CH₂Cl₂, and the extract was worked-up conventionally and concentrated to dryness. The residue was crystallized from dry benzene. The yields were 95–98 %.

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Pentaphenylcyclopentadiene, mp 250°C (Ref.² 248–250°C); ¹H NMR (C_6D_6 , 400 MHz), δ : 5.23 (s, 1 H, CH); 7.40–6.85 (m, 25 H, arom.).

1,2,5-Triphenyl-3,4(1,8-naphthylene)cyclopentadiene, mp 234°C. Mass spectrum, m/z (70 eV, direct inlet): $[M]^+$ 418. ¹H NMR (C₆D₆, 400 MHz), δ : 5.62 (s, 1 H, CH); 6.75–7.40 (m, 21 H, arom.).

Found (%): C, 94.65; H, 5.35. $C_{33}H_{22}$. Calculated (%): C, 94.70; H, 5.30.

References

- 1. L. D. Field, M. Ho. Kanthy, C. M. Lindall, A. F. Masters, and A. G. Webb, Aust. J. Chem., 1990, 98, 281.
- C. Janiak, H. Schuman, C. Stader, B. Wrackmeyer, and J. J. Zuckerman, *Chem. Ber.*, 1988, **121**, 1745.
- J. W. Chambers, A. J. Bashar, S. G. Bott, J. L. Atwood, and M. D. Rausch, Organometallics, 1986, 5, 1635.
- 4. W. Dithley, I. Horst, and W. Schommer, J. Prakt. Chem., 1935, 143, 189.

- 5. P. W. Reeves, and B. L. Williamson, Synth. Commun., 1987, 17, 1721.
- A. B. Sigalov, E. S. Petrov, L. F. Rybakova, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2615 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 2351 (Engl. Transl.)].
- A. B. Sigalov, E. S. Petrov, L. F. Rybakova, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2143 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, 35, 1955 (Engl. Transl.)].
- A. B. Sigalov, E. S. Petrov, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2386 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, 33, 2181 (Engl. Transl.)].
- 9. Z. Hou, H. Taniguchi, and Y. Fujivara, Chem. Lett., 1987, 305.
- T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, and M. Yokoyama, J. Org. Chem., 1984, 49, 3904.
- V. S. Abramov, and P. G. Mal'skii, *Zh. Obshch. Khim.*, 1939, 9, 1533 [J. Gen. Chem., 1939, 9 (Engl. Transl.)].
- C. F. H. Allen, and Van Allan, J. Org. Chem., 1952, 17, 845.

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PdCl₂-catalyzed hydrogenolysis of a C—O bond in monoaryl sulfates by sodium phosphinate in an aqueous alkaline medium

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The hydrogenolysis of the C–O bond in monoaryl sulfates by the action of an excess of NaH_2PO_2 in the presence of catalytic amounts of $PdCl_2$ and KOH is studied. The reaction proceeds chemoselectively with complete ester conversion to the corresponding arenes.

Key words: hydrogenolysis, monoaryl sulfates, palladium, catalysis.

The removal of OH groups from aromatic compounds is widely employed in synthetic organic chemistry for various purposes, including modification of natural substrates.¹⁻⁴ According to modern catalytic methods, phenols are first converted into such derivatives as esters of perfluorosulfonic acids,⁵⁻¹⁰ urethanes,^{11,12} tetrazoles,¹³ dialkyl phosphates,¹⁴ etc. On the one hand, the hydrogenolysis of such derivatives necessitates the use of anhydrous organic solvents and, on the other hand, a portion of the molecule, whose introduction required expensive reagents, is lost. It seemed attractive, therefore, to use derivatives of inorganic acids for the deoxygenation of phenols and to abandon organic solvents.

The hydrogenolysis of monoaryl sulfates in water in the presence of a Raney alloy has been described.¹⁵ The main drawback of this method is the use of large amounts of the Raney alloy, which produces the problem of utilizing the wastes containing Ni and Al. A method for the hydrogenolysis of an Ar-X bond, where X is Br or

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