LITERATURE CITED

1. N. N. Sukhanov (Suchanov), L. A. Yanovskaya, and V. P. Chetverikov, Abstracts of Papers of the 6th International Conference on Organic Synthesis (IUPAC), M. 1 (1986), A-455.
2. C. Chan and H. Huang, Synthesis, No. 6, 452 (1982).
3. N. N. Sukhanov, L. N. Trappel', V. P. Chetverikov, and L. A. Yanovskaya, Zh. Org. Khim., 21, 2503 (1985).
4. L. A. Yanovskaya and S. S. Yufit, Organic Synthesis in Two-Phase Systems [in Russian], Izd. Khimiya (1982).
5. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977).
6. K. Ya. Burshtein, Zh. Strukt. Khim., 28, No. 2, 3 (1987).

METATHESIS OF ALLYL CYANIDE IN THE PRESENCE OF A CATALYTIC SYSTEM CONTAINING TUNGSTEN HEXACHLORIDE AND 1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE

N. B. Bespalova, M. A. Bovina,
and V. M. Vdovin

UDC 542.97:547.339.2

Unsaturated nitriles undergo metathesis in the presence of heterogeneous $Re_2O_7/Al_2O_3-R_4Sn$ catalysts or homogeneous WCl_6-R_4Sn systems. The activity of $CH_2{=}CH(CH_2)_nCN$ increases with increasing n [1].

In previous work, we showed that the catalytic system containing WCl_6 and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) leads to the metathesis of linear and cyclic olefins [2] and of esters of unsaturated aliphatic acids and their cometathesis with α-olefins [3]. This catalytic system proved extremely efficient for the metathesis of unsaturated nitriles. Allyl cyanide undergoes metathesis as follows:

$$\underset{\text{(II)}}{2CH_2{=}CHCH_2CN} \xrightarrow{WCl_6 + (I)} \underset{\text{(III)}}{NCCH_2CH{=}CHCH_2CN} + C_2H_4$$

This reaction proceeds under rather mild conditions. The conversion of (II) at 60-70°C over 5-10 h is 45-55%. The selectivity for the formation of (III) is 80-90%.

EXPERIMENTAL

All the operations for the preparation of the reagents and catalyst were carried out in a dry argon atmosphere. Benzene solutions of the catalytic system components were used.

The products were analyzed by gas-liquid chromatography on a Chrom-5 chromatograph with a flame ionization detector using a 3 m × 3 mm column packed with OV-101 and chromato-mass spectrometry on an LKB-2091 spectrometer at 70 eV using a 70-m capillary column packed with OV-101. The WCl_6 sample was purified by sublimation in vacuum to remove more volatile oxychlorides at 150-160°C. Cyclobutane derivative (I) was obtained according to Sommer and Baum [4] with additional drying over sodium. A sample of (II) obtained according to a standard method [5] was distilled over P_2O_5 and stored over freshly roasted 5-Å molecular sieves.

Metathesis of (II). a) A sample of 50 mmoles (4 ml) (II), 1 mmole WCl_6 (3.7 ml solution in benzene), and 2 mmoles (I) (2.5 ml solution in benzene) were added in an argon stream to an ampul, subjected to previous heating in vacuum. The mixture was frozen with liquid nitrogen and evacuated to 0.001 mm Hg. The ampul was sealed and maintained at 60°C for 10 h.

A. V. Topchieva Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 920-921, April, 1988. Original article submitted July 9, 1987.

A sample of 15 ml ethanol was added to the ampul contents. The products were separated by distillation and analyzed by gas-liquid chromatography and chromato-mass spectrometry. The conversion of (II) was 53%. The selectivity relative to (III) was 82%. Product (III) was separated by crystallization, mp 72-74° (from ethanol) [6]. Mass spectrum of (III), m/z (intensity, %): 26(3), 39(18), 52(13), 66(100) $[M-CH_2C]^{+\cdot}$, 79(18), 106(20) $[M]^+$.

b) A sample of 50 mmoles (4 ml) (II), 0.5 mmole (1.85 ml solution in benzene) WCl_6, and 1 mmole (1.25 ml solution in benzene) (I) were added to an ampul. The reaction was carried out above 70°C over 6 h. The conversion of (II) was 51% and the selectivity relative to the formation of (III) was 85%.

CONCLUSIONS

The metathesis of allyl cyanide was carried out by the action of a catalytic system containing tungsten hexachloride by 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

LITERATURE CITED

1. R. H. A. Bosma, G. G. N. Van Den Aardweg, and J. C. Mol, J. Organomet. Chem., 280, 115 (1985).
2. N. S. Nametkin, V. M. Vdovin, É. D. Babich, et al., Dokl. Akad. Nauk SSSR, 225, 577 (1975).
3. V. M. Vdovin, N. B. Bespalova, and M. A. Bovina, Izv. Akad. Nauk SSSR, Ser. Khim., 2618 (1986).
4. L. H. Sommer and G. A. Baum, J. Am. Chem. Soc., 76, 5002 (1954).
5. Organic Syntheses [Russian translation], Vol. 1, Izd. Inos. Lit., Moscow (1949), p. 500.
6. US Patent No. 2,463,388; Chem. Abstr., 4286 (1949).

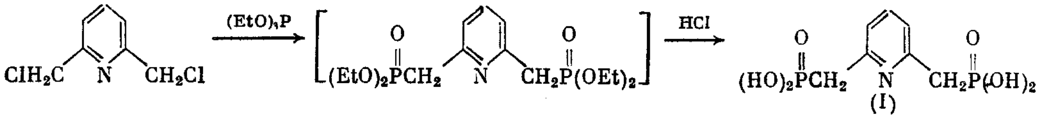
A NEW ORGANOPHOSPHORUS PYRIDINE COMPLEXONE — 2,6-BIS(DIHYDROXYPHOSPHORYLMETHYL)PYRIDINE

M. I. Kabachnik, Yu. M. Polikarpov,
G. V. Bodrin, and F. I. Bel'skii

UDC 541.49:547.821:547.26'118

Classical complexones contain acid and base groups. The base sites are usually nitrogen atoms, while the acid sites are carboxylic or phosphonic groups.

Organophosphorus complexones, containing a pyridine ring as the base site, have not been studied. In this regard, we synthesized and studied the acid-base and complexing properties of 2,6-bis(dihydroxyphosphorylmethyl)pyridine (I). The synthesis of this complexone was carried out by the Arbuzov reaction using 2,6-bis(chloromethyl)pyridine with excess triethyl phosphite and subsequent acid hydrolysis of the intermediate diphosphonate.



The reaction product is a crystalline compound which has good solubility in water but low solubility in ethanol and is insoluble in other organic solvents.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 921-924, April, 1988. Original article submitted July 4, 1987.