LETTERS TO THE EDITOR

REACTION OF THIOSEMICARBAZIDE WITH CYANOACETIC ESTER

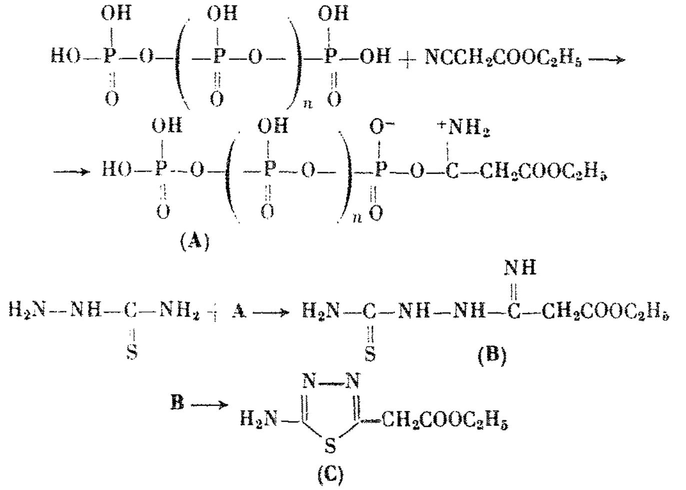
S. Sh. Shukurov, M. A. Kukaniev, I. M. Nasyrov,*
and R. A. Karakhanov

UDC 547.863.3.07

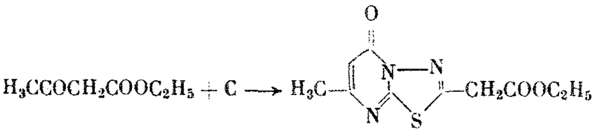
After Penner conversion into an iminoether, cyanoacetic ester becomes more reactive. This is confirmed by its reaction with thiosemicarbazide in boiling acetic acid medium with formation of 2-amino-1,3,4-thiadiazolyl-5-acetic acid ethyl ester (**C**) [1].

We found that cyanoacetic ester can be converted into a 1,3,4-thiadiazole derivative, by-passing the stage of formation of the iminoether. When thiosemicarbazide reacts with cyanoacetic ester and then with acetoacetic ester in polyphosphoric acid medium for 3-4 h at 95-100°C, previously undescribed 7-methyl-5-oxo-5H-1,3,4-thiadiazolo[3,2-a]pyrimidinyl-2-acetic acid ethyl ester (**1**) is formed with an 80% yield.

The reaction perhaps takes place by stages via the stage of addition of cyanoacetic ester to polyphosphoric acid (product **A**) [2] with subsequent transition into amidrazone **B** and cyclization into **C**:



Conversion of **C** into **1** takes place with the acetoacetic ester according to the scheme:



(1)

Compound **1** ($C_{10}H_{11}N_3SO_3$) is a crystalline white substance with mp = 86°C (chloroform:hexane, 1:1). IR spectrum (KBr, ν, cm^{-1}): 1693 (C=O, cycl.); 1717 (C=O, exocycl.); PMR spectrum ($CDCl_3$, δ, ppm): 6.20 s (1H, CH), 4.22 q (2H, CH_2), 4.07 s (2H, CH_2), 2.32 s (3H, CH_3), 1.25 t (3H, CH_3). The data from elemental analysis of **1** are in agreement with the calculated data.

---

*Deceased.

V. I. Nikitin Institute of Chemistry, Tadzhkistan Academy of Sciences, 734063 Dushanbe; I. M. Gubkin Institute of Oil and Gas, Moscow. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 5, pp. 1222-1223, May, 1992. Original article submitted July 25, 1991; revision submitted January 14, 1992.

1063-5211/92/4105-0965$12.50 ©1993 Plenum Publishing Corporation

LITERATURE CITED

1. V. V. Kiseleva, A. A. Gakh, and A. A. Faizil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2075 (1990).
2. E. N. Zil'berman, *Reactions of Nitriles* [in Russian], Khimiya, Moscow (1972).

AN EFFICIENT DEHYDROFLUORINATING SYSTEM FOR POLYVINYLIDENE FLUORIDE

Yu. P. Kudryavtsev, S. E. Evsyukov, and V. G. Babaev

UDC 678.743.3:542.944.6

Chemical dehydrohalogenation of halogen-containing polymers is an accessible and convenient method for preparation of carbon-chain polymers with a system of conjugated multiple bonds in the main chain, including carbyne [1]. The development of an efficient method of preparation of carbyne and articles made of it is still an urgent problem. It was previously shown that chemical dehydrohalogenation of polyvinylidene halides (PVDH) with an alcohol solution of a base causes the formation of a cumulene modification of carbyne [2]:

$$-(-CH_2-CX_2-)_{\overline{n}} \xrightarrow{-2nHX} =(=C=C=)_{\overline{\overline{n}}}, \text{ where } X = F, Cl, Br.$$

In the PVDH series, polyvinylidene fluoride (PVDF) is the most promising starting polymer for fabricating carbyne articles due to its better solubility. However, dehydrofluorination of PVDF takes place slowly due to the highest strength of the halogen–carbon bond in the order C–F > C–Cl > C–Br [3]. Addition of several polar solvents (DMSO, pyridine) to an alcohol solution of a base significantly accelerates the dehydrohalogenation reaction [1]. An efficient system, a mixture of a solution of KOH in ethanol with tetrahydrofuran (THF), was used in [2] for dehydrohalogenation of PVDH. The use of THF allowed conducting the dehydrohalogenation reaction relatively efficiently in soft conditions – at room temperature and even lower. However, in this case, too, dehydrofluorination of PVDH took place slowly: the degree of dehydrofluorination of the films was only 70% after 28 h.

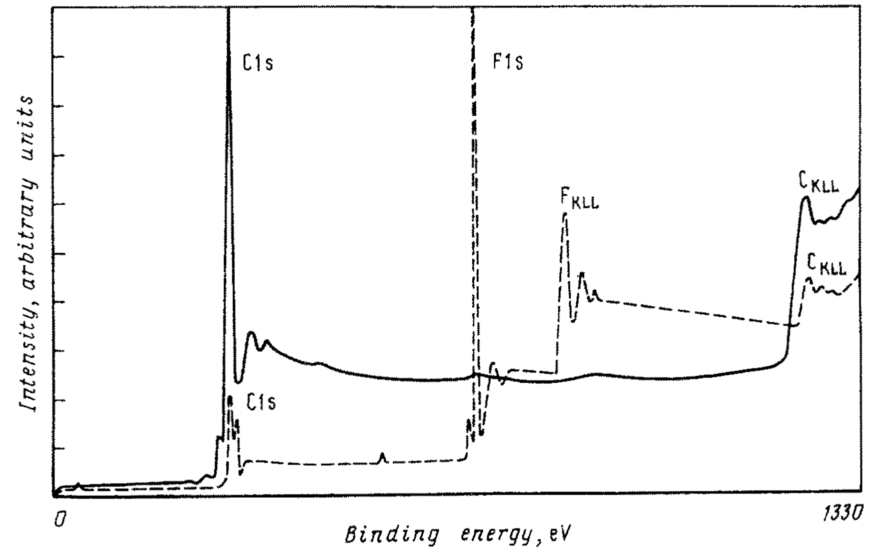


Fig. 1. Photoelectron spectra (ESCA) of the starting PVDF film (dashed line) and a film dehydrofluorinated for 1 h at 20°C (solid line).

A. N. Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, 117813 Moscow. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 5, pp. 1223-1225, May, 1992. Original article submitted November 5, 1991.

1063-5211/92/4105-0966$12.50 ©1993 Plenum Publishing Corporation