

4. V. A. Ditkin and A. P. Prudnikov, Integral Transformations and Operational Calculation [in Russian], Nauka, Moscow (1974).
5. G. É. El'kin, A. T. Melenevskii, and G. V. Samsonov, Vysokomol. Soedin., **B16**, 871 (1974).
6. E. Kučera, J. Chromatogr., **19**, 237 (1965).
7. L. Z. Vilenchik, V. I. Kolegov, and B. G. Belen'kii, Zh. Fiz. Khim., **46**, 1109 (1972).
8. P. P. Zolotarev and L. V. Radushkevich, Izv. Akad. Nauk SSSR, Ser. Khim., **1968**, 1906.
9. G. É. El'kin, A. T. Melenevskii, and G. V. Samsonov, in monograph: Molecular Liquid Chromatography, Abstracts of Papers [in Russian], Nauka, Chernogolovka (1979), p. 51.

REACTION OF TRIETHYLGERMYLLITHIUM WITH CARBOXYLIC

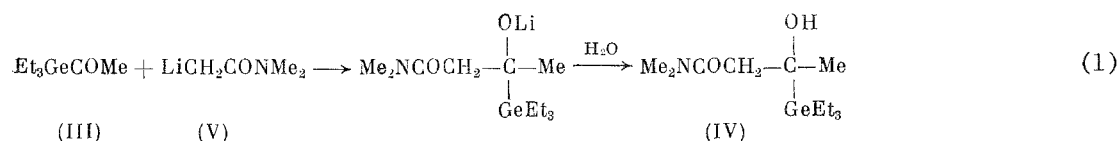
ACID N,N-DIALKYLAMIDES

D. A. Bravo-Zhivotovskii, S. D. Pigarev,
O. A. Vyazankina, I. D. Kalikhman,
and N. S. Vyazankin

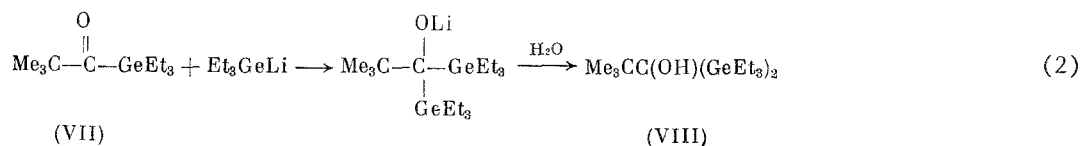
UDC 542.91:547.246:547.253.4:
547.298.1

It is known that organic Li compounds, when reacted with carboxylic acid N,N-dialkylamides of the RCH_2CONMe_2 series, attack the CO group to give ketones [1, 2] and (or) they metalate the CH_2 and $N-CH_3$ groupings [3, 4]. In the case of the N,N-dialkylbenzamides the regiospecific metalation of the ortho position of the benzene nucleus takes place [5, 6]. We found that the reaction of $Et_3GeLi(I)$ with N,N-diethylbenzamide in hexane at $\sim 20^\circ C$ is regioselective at the $C=O$ group and, after hydrolysis, leads to $Et_3GeCOPh$ in 88% yield. The o-metalation reaction is not realized under these conditions. When N,N-diethyltrifluoroacetamide is reacted with (I) the unexpected product (cf. [7]) is the diethylamide of triethylgermylcarboxylic acid, the first member of the amides of the $R_3GeCONR_2$ series.

When (I) is reacted with N,N-dimethylacetamide (II) in hexane the products isolated after hydrolysis were Et_3GeAc (III) and the dimethylamide of 3-hydroxy-3-(triethylgermyl)-butanoic acid (IV). Compound (III) is obtained either by the hydrolysis of the addition product of Et_3GeLi to the $C=O$ group of amide (II) (cf. [1, 2]) or by the heterolysis of the $N-CO$ bond in (II) using (I), as also occurs when $BuLi$ is reacted with N-substituted lactams with small rings [8, 9]. The formation of (IV) can be explained by a scheme that postulates the intermediate formation of the Li derivative of dimethylacetamide (V). It was shown by



special experiments that metalation of the acetyl fragment becomes the main process when amide (II) is reacted with Et_3GeLi in THF or with Et_3GeK in benzene. The subsequent addition to the reaction mixtures of either MeI or Me_3SiCl leads respectively to the N,N-dimethylamides of propionic and trimethylsilylacetic acid. Their yields are nearly quantitative. It is also known that (V) easily adds to the carbonyl group of aldehydes and ketones [10]. The N,N-dimethylamide of trimethylacetic acid (VI), which, in contrast to amide (II), lacks enolizable protons, reacts with (I) to give trimethylacetyl(triethyl)germane (VII) and 1,1-bis(triethylgermyl)-2,2-dimethyl-1-propanol (VIII). The latter is probably formed by reaction (2).



Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp. 949-951, April, 1982. Original article submitted July 29, 1981.

EXPERIMENTAL

All of the reactions were run in evacuated sealed ampuls. The PMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz), using TMS as the internal standard. The IR spectra were taken on a UR-20 instrument, and the GLC analysis was run on a Chrom-4 instrument, using a katharometer as the detector, helium as the carrier gas, and a 2 m × 1.5 mm metal column packed with 15% PMS-100 deposited on Chromaton N-AW.

Reaction of Triethylgermyllithium (I) with Dimethylacetamide (II). A mixture of 3.3 g of (I) and 1.7 g of (II) in 30 ml of hexane was stirred for 1.5 h at -20° , after which it was heated to 20° and decomposed with water. The organic layer was extracted with ether, and the extract was dried over MgSO_4 and then fractionally distilled to give 2.0 g (50%) of (III), bp 65° (8 mm), n_D^{20} 1.4583. Found: C 47.57; H 8.93; Ge 35.64%. $\text{C}_8\text{H}_{18}\text{GeO}$. Calculated: C 47.50; H 8.97; Ge 35.88%. Infrared spectrum (ν , cm^{-1}): 1657 ($\text{C}=\text{O}$). PMR spectrum (CCl_4 , δ , ppm): 0.86 m ($\text{C}_2\text{H}_5\text{Ge}$), 2.07 s (CH_3). We also isolated 1.0 g (18%) of (IV), bp 95° ($8 \cdot 10^{-2}$ mm), n_D^{20} 1.4872. Found: C 49.66; H 9.25; Ge 25.21; N 4.57%. $\text{C}_{12}\text{H}_{27}\text{GeNO}$. Calculated: C 49.71; H 9.39; Ge 25.04; N 4.83%. Infrared spectrum (ν , cm^{-1}): 1630 ($\text{C}=\text{O}$), 3400 (OH). PMR spectrum (CCl_4 , δ , ppm): 0.85 m ($\text{C}_2\text{H}_5\text{Ge}$), 1.12 s (CH_3-C), 2.78 s (CH_3-N), 2.85 s (CH_3-N), 2.20 d (CH_2 , $^2J = 16$ Hz), 2.32 d (CH_2^2 , $J = 16$ Hz).

In a similar manner, from (I) and amide (II) in THF, followed by the addition of a double excess of MeI, we obtained N,N-dimethylpropioamide and triethylgermane, which were identified by GLC. The respective yields were 86 and 89%.

N,N-Dimethylamide of Trimethylsilylacetic Acid (IX). A mixture of 4.0 g of Et_3GeK and 1.7 g of (II) in 30 ml of benzene was stirred for 1.5 h at $\sim 20^{\circ}\text{C}$. Then 4.3 g of Me_3SiCl was added and the mixture was stirred for another hour. After filtration and fractional distillation of the mixture we isolated 2.5 g (79%) of (IX), bp 55° (2 mm), n_D^{20} 1.4515 (cf. [11]).

Reaction of Triethylgermyllithium with N,N-Dimethylamide of Trimethylacetic Acid. A mixture of 3.2 g of (I) and 1.9 g of amide (VI) in 30 ml of hexane was stirred for 4 h at 20° . After hydrolysis the organic layer was dried over MgSO_4 . Fractional distillation of the mixture gave 1.1 g (30%) of ketone (VII), bp $49-51^{\circ}$ ($6 \cdot 10^{-2}$ mm), n_D^{20} 1.4581. Found: C 53.78; H 10.08; Ge 29.21%. $\text{C}_{11}\text{H}_{24}\text{GeO}$. Calculated: C 53.96; H 9.88; Ge 29.64%. Infrared spectrum (ν , cm^{-1}): 1640 ($\text{C}=\text{O}$). We also isolated 1.2 g (24%) of carbinol (VIII), bp $102-103^{\circ}$ ($6 \cdot 10^{-2}$ mm), n_D^{20} 1.5060. Found: C 50.09; H 9.49; Ge 39.32%. $\text{C}_{17}\text{H}_{40}\text{GeO}$. Calculated: C 50.33; H 9.94; Ge 39.79%. Infrared spectrum (ν , cm^{-1}): 1470 (OH).

Benzoyltriethylgermane. A mixture of 3.4 g of (I) and 2.7 g of N,N-diethylbenzamide in 30 ml of hexane was stirred for 4 h at $\sim 20^{\circ}$ and then hydrolyzed. After drying and fractional distillation of the organic layer we isolated 3.5 g (88%) of benzoyltriethyogermane, bp $86-87^{\circ}$ (0.07 mm), n_D^{20} 1.5318. Infrared spectrum (ν , cm^{-1}): 1630 ($\text{C}=\text{O}$) (cf. [12]).

N,N-Diethylamide of Triethylgermylcarboxylic Acid (IX). A mixture of 3.1 g of (I) and 2.7 g of N,N-diethyltrifluoroacetamide in 30 ml of hexane was stirred for 4 h at $\sim 20^{\circ}$ and then hydrolyzed. The organic layer was worked up in the usual manner to give 2.4 g (58%) of amide (IX), bp $68-70^{\circ}$ (0.08 mm), n_D^{20} 1.4776. Found: C 51.07; H 9.63; Ge 28.04; N 5.16%. $\text{C}_{11}\text{H}_{25}\text{GeNO}$. Calculated: C 50.83; H 9.70; Ge 27.93; N 5.39%. Infrared spectrum (ν , cm^{-1}): 1585 ($\text{C}=\text{O}$). PMR spectrum (CCl_4 , δ , ppm): 0.70 m ($\text{C}_2\text{H}_5\text{Ge}$), 2.40 m ($\text{C}_2\text{H}_5\text{N}$).

CONCLUSIONS

The reaction of Et_3GeLi with the N,N-dialkylamides of the benzoic, acetic, and trimethylacetic acids leads to the corresponding acyltriethylgermanes, RCOGeEt_3 , and the products of their transformation by the Li derivatives that are present.

LITERATURE CITED

1. R. P. Cassity, L. T. Taylor, and J. F. Wolfe, J. Org. Chem., **43**, 2286 (1978).
2. D. S. Owsley, J. M. Nelke, and J. J. Blomfield, J. Org. Chem., **38**, 901 (1973).
3. D. N. Grouse and D. Seebach, Chem. Ber., **101**, 3113 (1968).
4. W. Lubosch and D. Seebach, Helv. Chim. Acta, **63**, 102 (1980).
5. L. Barsky, H. W. Gschwend, J. McKenna, and H. R. Rodriguer, J. Org. Chem., **41**, 3651 (1976).
6. P. Beak and R. A. Brown, J. Org. Chem., **42**, 1823 (1977).
7. N. A. Zaitseva, E. M. Panov, and K. A. Kocheskov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, **1961**, 831.

8. S. Kano, T. Ebata, and S. Shibuya, *Chem. Pharm. Bull. (Tokyo)*, **27**, 2450 (1979).
9. E. R. Talaty and C. M. Untermohlen, *J. Chem. Soc. Chem. Commun.*, **1974**, 204.
10. R. P. Woodbury and M. W. Rathke, *J. Org. Chem.*, **42**, 1688 (1977).
11. I. E. Lutsenko, Yu. I. Baukov, A. S. Kostyuk, N. I. Savel'eva, and Y. K. Kysina, *J. Organometal. Chem.*, **17**, 241 (1969).
12. A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967).

REACTION OF DIPHENYLTHIOPHOSPHINOUS ESTERS WITH DIPHENYLCHLOROPHOSPHINE

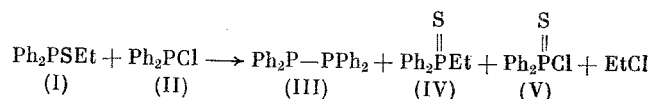
V. A. Al'fonsov, D. A. Pudovik,
É. S. Batyeva, and A. N. Pudovik

UDC 542.91:547.1'118

It is known [1, 2] that the esters of P(III) acids react with halophosphines by the Arbuzov reaction to give compounds with a phosphorus-phosphorus bond. Aminophosphines are also capable of adding to chlorophosphines, but in this case the reaction stops at the step of forming quasiphosphonium compounds [3]. The reaction of the thioesters of P(III) acids with halophosphines has not been studied. Only the reactions of the trithioesters with PCl_3 are known, which lead to an exchange of the substituents [4].

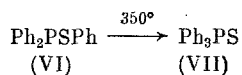
We studied the reaction of the ethyl ester of diphenylthiophosphinous acid (I) with diphenylchlorophosphine (II). The derivatives of the same acid were chosen so as to not complicate the reaction due to the exchange processes of the thioalkyl group with the halide.

In contrast to the oxygen esters of P(III) acids, the reaction with thiophosphinite (I) proceeds under drastic conditions (250°C , neat) and leads to the formation of a mixture of tetraphenyldiphosphine (III) with $\delta^{31}\text{P} - 16$ ppm, ethyldiphenylphosphine sulfide (IV) with $\delta^{31}\text{P} + 45$ ppm, and diphenylchlorophosphine sulfide (V) with $\delta^{31}\text{P} + 79.5$ ppm [5]. It should be mentioned that (II) does not react completely. In addition, small amounts of S-ethyl di-



phenyldithiophosphinate were detected by the ^{31}P NMR and TLC methods.

In contrast to this, the phenyl ester of diphenylthiophosphinous acid (VI) does not react with (II) even at 350° . Only the isomerization of (VI) to triphenylphosphine sulfide (VII) is observed under these conditions. The presence of (II) in the reaction mixture apparently has no effect on the isomerization process, since the heating of thiophosphinite (VI) to 350° in the absence of diphenylchlorophosphine also leads to the isomerization product.



EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a nonserial KCU-4 NMR instrument at an operating frequency of 10.2 MHz. The external standard was 85% H_3PO_4 . The PMR spectra were taken on a Varian T-60 spectrometer at an operating frequency of 60 MHz relative to TMS.

Reaction of Ethyl Diphenylthiophosphinite (I) with Diphenylchlorophosphine (II). A mixture of 7.5 g of (I) and 7.0 g of (II) was heated at 250° for 0.5 h, cooled, and 5 ml of benzene was added. On standing at 20° a product deposited from the mixture, which was recrystallized from ether to give 3.5 g (31%) of (III) with mp 121° (cf. [6]). PMR spectrum (CCl_4): δ 7.23-8.33 ppm. (C_6H_5); the mixed melting point was 120° . Fractional distillation of the

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp. 951-952, April, 1982. Original article submitted July 31, 1981.