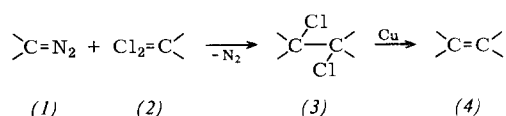


# Reactions of Diaryldiazomethanes with Halogeno Compounds [\*]

By Prof. Dr. A. Schönberg and Dipl.-Chem. E. Frese

Fakultät für Allgemeine Ingenieurwissenschaften  
der Technischen Universität Berlin (Germany)

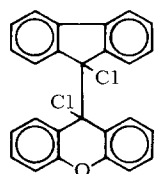
We have found that diaryldiazomethanes (1) in benzene or petroleum ether react briskly at room temperature without irradiation and without decomposition catalysts with some halogeno compounds, e.g. diaryldichloromethanes (2).



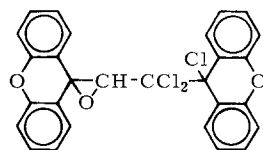
The 1,2-dichloroethanes (3) produced are readily dechlorinated with copper powder in boiling ligroin (100–140 °C) to give the corresponding ethylenes (4) in ca. 90 % yield.

For example, starting from diazofluorene and 9,9-dichloroxanthene we obtained a 75 % yield of 9-(*o*-biphenylenechloromethyl)-9-chloroxanthene (5), m.p. 176 °C, which was converted into *o*-biphenylenemethylenexanthene [1]. Again, bis-(4-methoxyphenyl)diazomethane and 9,9-dichloroxanthene gave rise to 9-[bis-(4-methoxyphenyl)chloromethyl]-9-chloroxanthene, m.p. 76 °C (from absolute petroleum ether, b. p. 60–70 °C under nitrogen), in ca. 50 % yield, and thence to 9-bis-(4-methoxyphenyl)methylenexanthene [2], m.p. 179 °C (from chloroform/ethanol). Treatment of the reaction product obtained from diazoxanthene and 9,9-dibromofluorene with copper powder also yielded *o*-biphenylenemethylenexanthene.

Diazoxanthene is very reactive; it reacts exothermally with excess CCl<sub>4</sub> at room temperature without irradiation to give 9,9'-dichlorobixanthyl, m.p. 203 °C (from petroleum ether, b.p. 90–100 °C), in ca. 35 % yield. With copper powder it is converted almost quantitatively into the known derivative bixanthylene. Its reaction with excess CHCl<sub>3</sub> goes just as easily; the 9-chlorobixanthyl formed is converted by ethanol into 9-ethoxybixanthyl, m.p. 145 °C (from ethanol), in ca. 50 % yield.



(5)



(6)

Diazofluorene and diphenyldiazomethane do not react with CHCl<sub>3</sub> or CCl<sub>4</sub> under the above conditions. Benzylphenyldiazomethane is somewhat more reactive and decomposes to form over 90 % ketazine.

Diazoxanthene and chloral combine in benzene with evolution of nitrogen to yield a compound C<sub>28</sub>H<sub>17</sub>Cl<sub>3</sub>O<sub>3</sub> (decomp. above 180 °C), for which we propose formula (6). The infrared spectrum of (6) in Nujol or CCl<sub>4</sub> shows no carbonyl band.

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German version: Angew. Chem. 76, 343 (1964)

[\*] A recent publication by H. Reimlinger, Chem. Ber. 97, 339 (1964), has induced us to report some of our results.

[1] A. Schönberg and M. M. Sidky, J. Amer. chem. Soc. 81, 2262 (1959).

[2] We also obtained 9-bis-(4-methoxyphenyl)methylenexanthene by the reaction of bis-(4-methoxyphenyl)diazomethane with xanthone, the ethylene sulfide formed being desulfurized with copper powder.

# Synthesis of Penicillamine Amide and Penicillamine Thioamide from Thiazolidine-4-carboxamides and -4-thiocarboxamides

By Prof. Dr. F. Asinger, Dr. W. Schäfer, and  
Dipl.-Chem. E.-Chr. Witte

Institut für Technische Chemie  
der Technischen Hochschule Aachen (Germany)

Gaseous hydrogen cyanide adds on smoothly at room temperature to the azomethine bond of many Δ<sup>3</sup>-thiazolines [1,2]. The stability of the resultant novel thiazolidine-4-carbonitriles (1) depends both on their purity and the number and type of substituents on the 2- and 4-positions; they are invariably stable in the form of their hydrochlorides (Table 1).

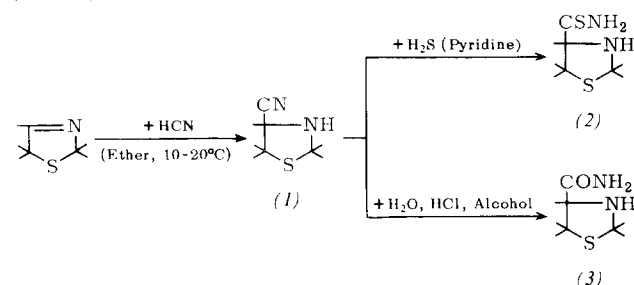
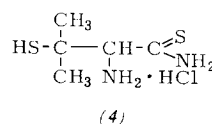


Table 1. Thiazolidine-4-carbonitriles (1), -thiocarboxamides (2), and -carboxamides (3).

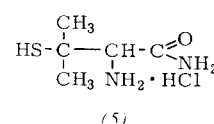
Δ <sup>3</sup> -Thiazoline	(1)		(2)		(3)	
	Yield [%]	m. p. [°C]	Yield [%]	m. p. [°C]	Yield [%]	m. p. [°C]
5,5-Dimethyl-	88	57,5 (144) [*]	79	162	72	177–178 (222)
2,5,5-Trimethyl-	92	58	74	171		
2-Isopropyl-5,5-dimethyl-	96	31 (253)	62	117	98	97 (236)
2-Phenyl-5,5-dimethyl-	88	109 (167–169)	25	155		
2,2,4-Trimethyl-	93	54			76	148 (236)
2,2,5,5-Tetramethyl-	94	73 (171)	54	171	47	148 (204–205)
2,2-Diethyl-5,5-dimethyl-	97	37	34	174		
2,2-Pentamethylene-5,5-dimethyl-	92	54 (185)	26	177	74	138 (232)
2,2,4-Triethyl-5-methyl-	94	70				

[\*] In parentheses: m. p. of the hydrochloride.

The nitriles react with H<sub>2</sub>S at 0–10 °C to give the previously unknown, colorless thiazolidine-4-thiocarboxamides (2); the yields increase with decreasing substitution at the 2-position (Table 1). H<sub>2</sub>S has not yet been added onto 4-substituted nitriles. Treatment of the nitriles with aqueous-alcoholic HCl gives the hydrochlorides of thiazolidine-4-carboxamides (3) (cf. Table 1). Hydrolytic ring opening of the thioamides (2)



(4)



(5)

with 2N HCl gives high yields of α-amino-β-mercaptothioamides and oxo compounds. Starting from 2,2,5,5-tetramethylthiazolidine-4-thiocarboxamide, we obtained a quantitative yield of the previously inaccessible compound α-

amino- $\beta$ -mercaptothioisovaleramide as its hydrochloride (4) (penicillamine thioamide hydrochloride, m.p. 169 °C). Similarly, hydrolysis of 2,2,5,5-tetramethylthiazolidine-4-carbonitrile hydrochloride led via the 4-carboxamide to the previously unknown derivative  $\alpha$ -amino- $\beta$ -mercaptoisovaleramide hydrochloride (5) (penicillamine amide hydrochloride, m.p. 235 °C) in quantitative yield.

Received, February 14th, 1964 [Z 666/489 1E]  
German version: Angew. Chem. 76, 273 (1964)

[1] F. Asinger and M. Thiel, Angew. Chem. 70, 667 (1958).

[2] Cf. [1], p. 677.

## Preparation of Silylgermanes

By Prof. Dr. P. Royen and Dipl.-Chem. C. Rocktäschel

Institut für anorganische Chemie  
der Universität Frankfurt/Main (Germany)

Attack by 5–6 N HCl on calcium germanide yields an amorphous lower germanium hydride [1] and a mixture of volatile germanium hydrides. Decomposition of the analogous silicide proceeds correspondingly [2]. The formation of mixed volatile hydrides on decomposing solid solutions of the type  $\text{Ca}_2(\text{Ge},\text{Si})$  and  $\text{Ca}(\text{Ge},\text{Si})$  was to be expected.

Homogeneous crystalline solid solutions of germanium and silicon in the ratio 1:1 were produced by melting the elements (Ge: 99.999 % pure, Si: 99.999 % pure from Messrs. Schuchardt) together and tempering at 1050–1100 °C for 30 days [3]. This alloy was mixed with the stoichiometric amount of calcium (99.85 % pure from Messrs. Schuchardt), and the mixture welded into a steel crucible [4], evacuated, and fused by heating briefly to 1200 °C. The X-ray patterns of the mixed crystals thus obtained were in accordance with those of the isotopic phases  $\text{CaSi}$  and  $\text{CaGe}$  [5] or  $\text{Ca}_2\text{Si}$  and  $\text{Ca}_2\text{Ge}$  [6]. For the reaction, 5–6 N HCl was slowly dropped onto the solid solution with cooling in an evacuated apparatus.

Examination of the gases developed by mass spectrometry [7] showed that  $\text{Ca}_2(\text{Ge},\text{Si})$  gave rise to the already known volatile hydrides  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ ,  $\text{Si}_3\text{H}_8$ ,  $\text{GeH}_4$ ,  $\text{Ge}_2\text{H}_6$ ,  $\text{Ge}_3\text{H}_8$ , and  $\text{SiGeH}_6$  [8] together with the hitherto unknown mixed hydrides  $\text{Si}_2\text{GeH}_8$  and  $\text{SiGe}_2\text{H}_8$ . The same hydrides were obtained together with  $\text{Si}_4\text{H}_{10}$  from  $\text{Ca}(\text{Ge},\text{Si})$ .

Received, January 20th and February 17th, 1964 [Z 663/492 1E]  
German version: Angew. Chem. 76, 302 (1964)

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[2] R. Schwarz and F. Heinrich, Z. anorg. allg. Chem. 221, 277 (1935).

[3] H. Stöhr and W. Klamm, Z. anorg. allg. Chem. 241, 305 (1939).

[4] A. Weiss and G. Rocktäschel, Z. anorg. allg. Chem. 307, 1 (1960).

[5] P. Eckerlin, H. J. Meyer, and E. Wölfel, Z. anorg. allg. Chem. 281, 322 (1955).

[6] P. Eckerlin and E. Wölfel, Z. anorg. allg. Chem. 280, 321 (1955).

[7] We wish to thank Dr. W. Mosch, Institut für physikalische Chemie, Frankfurt/Main, for the mass-spectrometric identification of the volatile hydrides.

[8] E. J. Spanier and A. G. MacDiarmid, Inorg. Chem. 2, 215 (1963); preparation from  $\text{SiH}_4$  and  $\text{GeH}_4$  by silent electrical discharge.

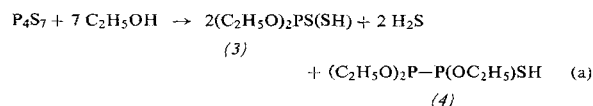
## Alcoholysis of Tetraphosphorus Heptasulfide $\text{P}_4\text{S}_7$

By Dipl.-Chem. H. Petschik and Prof. Dr. E. Steger

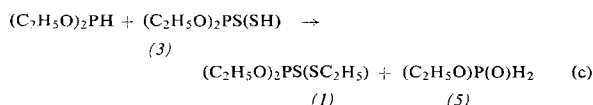
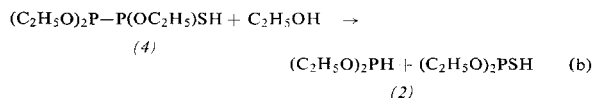
Institut für Anorganische und Anorganisch-Technische Chemie und Institut für Spezielle Analytische Chemie der Technischen Universität Dresden (Germany)

The esters  $(\text{RO})_2\text{PSSH}$ ,  $(\text{RO})_2\text{PSH}$ , and  $(\text{RO})_2\text{PS}(\text{SR})$  plus  $\text{H}_2\text{S}$  and some  $\text{PH}_3$  have been described as the products of alcoholysis of  $\text{P}_4\text{S}_7$  [1]. The NMR spectrum of the reaction mixture of  $\text{P}_4\text{S}_7$  and n-butanol displays 9 signals [2]. We allow-

ed  $\text{P}_4\text{S}_7$  to react in  $\text{CS}_2$  with ethanol at  $\approx 20^\circ\text{C}$  and analysed the mixture quantitatively by thin-layer chromatography.  $(\text{C}_2\text{H}_5\text{O})_2\text{PS}(\text{SC}_2\text{H}_5)$  (1) and  $(\text{C}_2\text{H}_5\text{O})_2\text{PSH}$  (2) were found to be secondary products. According to our investigations, approximately two atoms of sulfur are split off per  $\text{P}_4\text{S}_7$  as  $\text{H}_2\text{S}$ ;  $(\text{C}_2\text{H}_5\text{O})_2\text{PS}(\text{SH})$  (3) is immediately detectable in the infrared spectrum and accounts initially for about half of the phosphorus in solution; hence we consider the main reaction to be:



$O,O,O'$ -Triethyl diphosphonothioate (4) is at present only characterized by its position on chromatograms, sensitivity towards water, and strong reducing properties; it decomposes within a few hours. As (4) decomposes, the proportion of (2) increases until it accounts for nearly one-quarter of the total phosphorus. Ester (1) attains this level only after 1–2 days. A substance must therefore be formed by cleavage of (4) which alkylates (3) to (1), for ethanol does not react with (1) under these conditions. From chromatograms and infrared spectra we assume that reactions (b) and (c) occur.



$(\text{C}_2\text{H}_5\text{O})\text{P}(\text{O})\text{H}_2$  (5), which is unstable at room temperature [3], accounts for the formation of  $\text{PH}_3$ ; the proportion of 5–7 % [4] of the total phosphorus found in this form agrees with the maximum amount of 8.33 % to be expected from (5). The other disproportionation product  $(\text{C}_2\text{H}_5\text{O})_2\text{POH}$  (6) occurs as an impurity that went unrecognized in most of the preparations of (2) described, which have  $\eta_{\text{sp}}^0 < 1.4695$  [1, 5] and infrared bands at 550 and 1270  $\text{cm}^{-1}$  [6]. It can be isolated from (2) by extraction with water; (2) and (6) are difficult to separate by distillation. In this way, we obtained about 98 %  $(\text{C}_2\text{H}_5\text{S})_2\text{PSH}$  (2), b.p. 72.5 °C/13.5 mm, with the refractive index specified. During the alcoholysis, water present converts (4) into a more strongly polar substance; the yield of (2) falls off correspondingly. This occurs particularly during methanolysis, since the complete esterification of  $(\text{CH}_3\text{O})_2\text{PS}(\text{SH})$  by excess methanol produces water.

The alcoholysis of  $\text{P}_4\text{S}_7$  produces varying yields ( $\leq 6\%$ ) of a bright yellow, finely powdered substance with  $\text{P}:\text{S} = 1:1$ ; this is probably identical with the  $(\text{PS})_x$  of Kuchen and Beckers [7]. This yellow substance, probably mixed with unreacted  $\text{P}_4\text{S}_7$ , appears to have been taken for sulfur by several authors [5, 8].

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German version: Angew. Chem. 76, 344 (1964)

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