

The evidently electrophilic attack of dimethylallyl pyrophosphate at the weakly reactive 4-position of the indole nucleus is surprising. The formation of the C ring by linking of an allylic C-atom with the α -position of an amino-acid is equally unusual. Whether this linkage takes place in (I) or (after decarboxylation) in the amine remains to be proved.

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[*] Dedicated to Prof. Dr. G. Wittig on the occasion of his 65th birthday.

[1] For literature summaries see: A. J. Birch et al., J. chem. Soc. (London) 421 (1962); H. Plieninger et al., Liebigs Ann. Chem. 642, 214 (1961).

[2] Grateful acknowledgement is tendered to the Sandoz AG., Basel (Switzerland), for the supply of the fungus strain and advice on its culture.

[3] A. Stoll et al., Helv. chim. Acta 37, 1815 (1954).

Combination of Thin-Layer Chromatography and Mass Spectrography

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Mass spectra can be obtained directly from samples of thin-layer chromatograms of condensed aromatic compounds, heterocycles, steroids, carbohydrate derivatives, amino acids and peptides.

In the structural analysis of organic compounds, mass spectrometry [1] with the usual experimental set-up (introduction of the test sample into the ion-source from a storage vessel, with or without an injection mechanism) can be applied only to substances of relatively high volatility. Less volatile compounds must be directly introduced into the ion source, where they are vaporized. However, this latter procedure [2] leads to strong "memory" effects and to a reduction in the resolving power of the mass spectrometer. In a CH-4 mass spectrometer [*] with a solid ion source the ionization chamber of the ion-source can be interchanged by means of a vacuum lock. The substance to be examined is placed in a small glass tube, 10 mm long and about 1 mm in diameter, and the open end is drawn into a capillary. The tube is fastened in the ionization chamber in such a manner that the substance sublimates directly into the electron beam. Thus, the resolving power is unaffected. Contamination of the ion source is mainly restricted to the easily cleaned ionization chamber. It is however a disadvantage that the temperature of the ion-source cannot be regulated and that the normal operating temperature is 150–200°C. The method can be applied to substances which are thermally stable at 150–200°C, and at this temperature possess a vapor pressure of about 10^{-7} mm Hg. We were able to obtain mass spectra of alicyclic carboxylic acids, sugar derivatives, and acylated amino acids and peptides [3]. Substances adsorbed on silica gel may be used directly. The background spectrum caused by silica gel and residual solvent does not interfere in the region of high masses, important for structure determinations. Several μg of substance is required; however, the ratio of substance to silica gel must be at least 1:100. This ratio is achieved in the sharp and intense spots of thin-layer chromatograms.

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[*] Made by the Atlas Mess- und Analysen-Technik GmbH., Bremen (Germany).

[1] K. Biemann, Angew. Chem. 74, 102 (1962).

[2] R. I. Reed, W. K. Reid and J. M. Wilson: Symposium on Mass Spectrometry. Oxford 1961.

[3] The experiments were carried out in collaboration with Dipl.-Chem. H. Scharmann. The results will be reported in detail elsewhere.

The Reaction of Chlorosilanes with Divers' Solutions

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Silyl derivatives of NH_3 , methylamine or dimethylamine are mostly obtained by the reaction of halogenosilanes with the amines in an inert solvent [2]; hexamethyldisilazane, too, can be prepared by addition of trimethylchlorosilane to liquid NH_3 [3]. It is more convenient, however, to allow chlorosilane to react with Divers' solutions (ammonium salts in amines) [4] at normal pressure and in an ice-water bath. Two layers are obtained; the upper is nearly pure aminosilane, the lower contains the ammonium salts dissolved in excess amine. The silylamine can be recovered by decantation, or separation of the layers in a funnel. Using this very simple method, hexamethyldisilazane, the trimethylsilyl derivatives of methylamine and trimethylsilyldimethylamine were obtained in yields amounting to 80%, 83% and 84%, respectively.

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[1] 11th. Communication on the Si-N bond. 10th. Communication: K. Rühlmann, U. Kaufmann, and D. Knopf, J. prakt. Chem., in press.

[2] R. O. Sauer, J. Amer. chem. Soc. 66, 1707 (1944).

[3] R. O. Sauer and R. H. Hasek, J. Amer. chem. Soc. 68, 243 (1946); J. E. Noll, J. L. Speier, and B. F. Daubert, *ibid.* 73, 3867 (1951).

[4] E. Divers, Philos. Trans. Roy. Soc. (London) 163, 359 (1873).

Bistrifluoromethylphosphorus Derivatives of Transition Metal Carbonyls

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Perfluoroalkylphosphorus derivatives of transition metals have been previously described only with respect to nickel tetracarbonyl [1], e.g., $(\text{CF}_3)_3\text{PNi}(\text{CO})_3$, $[(\text{CF}_3)_3\text{P}]_2\text{Ni}(\text{CO})_2$ and $(\text{CO})_3\text{NiP}(\text{CF}_3)_2-\text{P}(\text{CF}_3)_2\text{Ni}(\text{CO})_3$. In these compounds, and by analogy to the bonding of the carbonyl groups, a phosphorus-nickel donor σ -bond through the phosphorus 3s-electron pair, and additional back-donation between the 3d-level of the nickel and the empty 3d-shell of the phosphorus ($d\pi-d\pi$ portion), are assumed [2].

By reaction of bistrifluoromethyliodophosphine with transition metal carbonyls, we have now succeeded in preparing perfluoromethylphosphorus derivatives which evidently contain a pure phosphorus-metal σ -bond (*cf.*, alkyl- and aryl-phosphine complexes of palladium, nickel and cobalt [3]).

The compound $\text{Mn}_2(\text{CO})_8\text{P}(\text{CF}_3)_2\text{I}$ (orange-red crystals) was isolated as the only reaction product resulting from the interaction of manganese carbonyl (1 mole) with bistrifluoromethyliodophosphine (1 mole) at 120°C in a sealed tube and in the absence of solvent. The product was separated, together with a small amount of $\text{Mn}_2(\text{CO})_{10}$, when the yellow-red crystalline mass resulting from an 18 hr. reaction was fractionally sublimed in high vacuum at 40–50°C. During the reaction, 1.8 moles of CO were liberated for each mole of manganese carbonyl.

The infrared spectrum shows carbonyl frequencies at 2101 cm^{-1} (s) [*], 2045 cm^{-1} (vs), 2009 cm^{-1} (s) and 1985 cm^{-1} (sh) as well as CF-absorptions at 1175 cm^{-1} (s), 1138 cm^{-1} (s), 1127 cm^{-1} (s) and 1102 cm^{-1} (m) which in contrast with those of bistrifluoromethyliodophosphine are shifted to lower wavenumbers. Phosphorus and iodine are envisaged as bridging atoms in the binuclear complex since the spectrum excludes