Vinylaluminum Compounds¹

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Vinyl-aluminium-Verbindungen können aus Aluminium-halogeniden, Aluminium-Metall oder -hydrid und einer Vinyl-Grignard-Verbindung oder einer anderen vinylierenden Substanz (Divinyl-quecksilber, Vinyl-alkalimetall-Verbindungen) gewonnen werden. Das Trivinyl-aluminium-tetrahydrofuran-Addukt entsteht in bis zu 40-proz. Ausbeute aus AlCl_3 und überschüssigem Vinyl-magnesiumchlorid in Tetrahydrofuran. Lösungsmittel-freies Trivinyl-aluminium erhält man aus granuliertem Al-Metall und Divinyl-quecksilber in Pentan. Beim Stehen bei Raumtemperatur polymerisiert es allmählich. Mit Äther bildet sich das Ätherat, $(\text{C}_2\text{H}_5)_3\text{Al} \cdot (\text{C}_2\text{H}_5)_2\text{O}$, mit Trimethylamin der Komplex $(\text{C}_2\text{H}_5)_3\text{Al} \cdot \text{N}(\text{CH}_3)_3$, der sich auch aus $\text{AlCl}_3 \cdot \text{N}(\text{CH}_3)_3$ und Vinyl-natrium (aus Divinyl-quecksilber und einer Na-Suspension) in Pentan oder aus $\text{AlH}_3 \cdot \text{N}(\text{CH}_3)_3$ mit Divinyl-quecksilber in Äther gewinnen läßt. Die letztere Reaktion wird allgemein von Verbindungen mit Al-H-Bindungen gegeben. So entsteht aus LiAlH_4 und einem Überschuß von Divinyl-quecksilber $\text{LiAl}(\text{C}_2\text{H}_5)_4$. Bei Einwirkung von Pyridin auf $(\text{C}_2\text{H}_5)_3\text{Al}$ oder $(\text{C}_2\text{H}_5)_3\text{Al} : \text{O}(\text{C}_2\text{H}_5)_2$ bildet sich das Addukt $(\text{C}_2\text{H}_5)_3\text{Al} : \text{NC}_5\text{H}_5$.

Results

Since the first preparation of vinyl Grignard reagents by NORMANT², quite a number of vinyl-metallics have been prepared. Recent reviews^{3–5} here and abroad have reflected the great interest that exists in this area. Although a large number of vinylboron derivatives have been characterized^{6–8} especially by STONE and coworkers⁹, and vinyl-gallium¹⁰ and vinylthallium¹¹ derivatives have been mentioned, no vinylaluminum compounds have previously been reported. This paper describes the preparation of some vinylaluminum compounds.

One of the most easily accessible vinylaluminum derivatives is trivinylaluminum-tetrahydrofuranate, $(\text{CH}_2=\text{CH})_3\text{Al} : \text{O}(\text{CH}_2)_4$. This compound is formed when an excess of vinylmagnesium bromide² or vinylmagnesium chloride¹² is reacted with an aluminum halide in tetrahydrofuran. The selection of the

Grignard compound to be used is quite critical. Reaction temperature and reaction time also influence the yield. The best yields are obtained from aluminum trichloride and vinylmagnesium chloride. Trivinylaluminum-tetrahydrofuranate is very sensitive to air and moisture. Even with traces of oxygen or water, dense smoke is formed; larger amounts are pyrophoric. However, the compound can be distilled without too great a decomposition at reduced pressure ($\sim 10^{-3}$ mm Hg). If the trivinylaluminum-tetrahydrofuranate is heated at atmospheric pressure, it decomposes, giving off tetrahydrofuran and forming an orange-red transparent polymer which is somewhat soluble in hydrocarbons and ether. In some cases, this polymer is no longer reactive to water.

Treatment of the trivinylaluminum-tetrahydrofuranate with trimethylamine or pyridine yields the trivinylaluminum-trimethylamine or the trivinylalu-

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⁹ F. E. BRINCKMAN and F. G. A. STONE, Chem. and Ind. **1959**, 254; F. E. BRINCKMAN and F. G. A. STONE, J. Amer. chem. Soc. **82**, 6218 [1960]; T. T. COYLE and F. G. A. STONE, J. Amer. chem. Soc. **82**, 6223 [1960]; H. D. KAESZ, S. L. STAFFORD and F. G. A. STONE, J. Amer. chem. Soc. **81**, 6336 [1959]; F. E. BRINCKMAN, Ph. D. THESIS, Harvard University, 1960.

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minum-pyridine complex, respectively. This latter compound is the only solid adduct of the several known for $(\text{CH}_2=\text{CH})_3\text{Al}$. Its isolation in pure form is simplified by easy sublimation under vacuum. When exposed to air it quickly forms a liquid, sticky material as it loses pyridine and ethylene. It appears to be considerably more stable toward polymerization than some of the other adducts of $(\text{CH}_2=\text{CH})_3\text{Al}$, as was shown by an unchanged melting point after two months of storage at room temperature. Pyridine will displace diethyl ether and tetrahydrofuran from their trivinylaluminum adducts, as would be expected.

A number of reactions known in organo aluminum chemistry permit the preparation of solvent-free alkyl aluminum compounds. The first reaction investigated was used in 1865 by BUCKTON and ODLING¹³, who reacted dialkylmercury compounds with aluminum metal. When a mixture of divinylmercury^{14-16, 11} and aluminum metal granules was heated to about 45 °C, an extraordinary spontaneous decomposition occurred. This reaction was quite contrary to that expected, since one has to heat dimethylmercury or diethylmercury to about 100 °C to obtain a good yield. However, the somewhat violent reaction proceeds quite readily when a solvent such as pentane, hexane, or cyclohexane is used:

The reaction may also be carried out in diethyl ether. In this case, of course, trivinylaluminum-etherate is formed. Even the solution of the trivinylaluminum in pentane is extremely reactive. If the solution of trivinylaluminum is allowed to stand for some time at room temperature, a glass-like polymer begins to precipitate. Purification and distillation of trivinylaluminum are very difficult after the solvent has been removed. If the amount of crude vinylaluminum subjected to fractionation is not big enough, complete polymerization takes place. The boiling point of the pure material is 55 °C (1 mm

Hg), which is somewhat higher than expected. This may be due to some polymerization.

Since most of the lower members of the trialkylaluminum series have been shown to exist in dimeric form in benzene solutions¹⁷, molecular weight measurements were made on $(\text{CH}_2=\text{CH})_3\text{Al}$ to determine whether or not it also was dimeric in solution. Molecular weight determinations that were carried out immediately after the preparation always yielded a figure higher than that of the expected dimer. Immediately after preparation, the lowest value found was 284.5; after 1 hr, the molecular weight of the same solution was determined to be 558. The calculated values for the trimer and pentamer are 325 and 540 respectively.

After additions of diethyl ether to the trivinylaluminum solution, the etherate $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{C}_2\text{H}_5)_2$ was isolated. With pyridine, the complex $(\text{CH}_2=\text{CH})_3\text{Al}:\text{C}_6\text{H}_5\text{N}$ is formed; and with trimethylamine, $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$.

Other methods of preparing the trivinylaluminum-trimethylamine adduct are the reaction of aluminum trichloride trimethylamine with vinylsodium in pentane or ether (synthesized from divinylmercury and a sodium dispersion⁸) or the reaction of aluminum hydride trimethylamine with divinylmercury in ether. This latter reaction mentioned is a general one and is valid for all aluminum hydrogen bonds¹⁸. Thus, the aluminum hydrogen bond in lithium aluminum hydride or in aluminum hydride and the addition compounds with Lewis bases can be vinylated quite easily with divinylmercury:

For instance, if one adds a slight excess of divinylmercury to $\text{AlH}_3:\text{N}(\text{CH}_3)_3$, a vigorous reaction occurs, hydrogen gas is given off, and a mud of mercury begins to settle. After the mixture is boiled at reflux temperature for about two hours, the mercury is filtered off, the ether is removed, and a white substance remains. This material may be purified fur-

¹³ G. B. BUCKTON and ODLING, *Liebigs Ann. Chem. Supl.* **4**, 109 [1865].

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¹⁶ G. F. REYNOLDS, R. E. DESSY and H. H. JAFFE', *J. org. Chemistry* **23**, 1217 [1958].

¹⁷ K. S. PITZER and M. S. GUTOWSKY, *J. Amer. chem. Soc.* **68**, 2204 [1946].

¹⁸ T. G. TRAYLOR, *Chem. and Ind.* **1959**, 1233, reported a reaction between LiAlH_4 and $(\text{C}_6\text{H}_5)_2\text{Hg}$ to yield $\text{LiAl}(\text{C}_6\text{H}_5)_4$. Parallel to our investigations, reactions of the type reported here were carried out by J. K. RUFF, Rohm & Haas Co., Huntsville, Alabama. J. K. RUFF, also synthesized $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$ among other trialkylaluminum derivatives. His results confirm the work described herein.

ther by high vacuum distillation. Some decomposition in form of polymerization occurs, but the analysis of the purified material checks very well with the values for trivinylaluminum-trimethylamine, and the infrared spectrum of this material is the same as that of trivinylaluminum-trimethylamine prepared by other methods. When this substance is hydrolyzed, no more hydrogen is evolved and the equivalent amount of ethylene is formed and can be measured. Lithium aluminum hydride reacts in the same way. In this case, lithium aluminum tetravinylate is formed:

Both reactions proceed quite smoothly. The hydrogen evolved in this reaction is a good measure for its completion.

The content in vinyl groups can be influenced and varied by the amount of vinylation reagent which is added to the hydride. Using a certain stoichiometric amount, for instance, of divinylmercury to aluminum hydride trimethylamine, one obtains monovinylaluminum-hydride-trimethylamine $(\text{CH}_2=\text{CH})\text{AlH}_2:\text{N}(\text{CH}_3)_3$, a white material that may be recrystallized from ether. Attempted sublimation will lead to polymerization.

Experimental¹⁹

Trivinylaluminum-Tetrahydrofuranate

In a 2-liter, 3-neck flask, fitted with a stirrer, dropping funnel, dry ice condenser, and gas inlet tube, 156 g (1.8 mole) of vinylmagnesium chloride in 700 ml freshly distilled tetrahydrofuran (THF) was prepared. Experience has shown that this Grignard reagent can be prepared fastest when the temperature is not allowed to drop below 55 °C at any time. After formation of the Grignard, a solution of 66.8 g (0.5 mole) of AlCl_3 in 600 ml of THF prepared at 0 °C was added dropwise with stirring while cooling with an ice bath. Upon completion of the addition, the reaction mixture was heated to 50–60 °C for 48 hrs. The solution was then cooled to 0 °C and filtered under N_2 into a flask for distillation. The THF was removed in vacuum until about 300 ml remained. At this time 250–300 ml of paraffin oil (distilled from LiAlH_4) was added, and distillation continued. Upon removal of the solvent 29.0 g (32%) of $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{CH}_2)_4$ distilled over at 86 °C (2 mm Hg).

Anal. calcd. for $\text{C}_{10}\text{H}_{17}\text{OAl}$:

C 66.64 H 9.51 Al 14.96.

Found: C 66.46 H 9.62 Al 14.99.

Trivinylaluminum

To 150 ml of pentane in a Minilab apparatus (Ace Glass Inc.) equipped with stirrer, dropping funnel and reflux condenser, 6 g (0.25 mole) of aluminum metal (Fisher Chemicals, granular, 20–30 mesh) was added, together with 2 g of divinylmercury. The mixture was then heated to reflux and stirred until the first traces of metallic mercury were deposited on the aluminum. The reaction flask was then cooled to 0 °C and maintained at this temperature during the course of the reaction. Another 83 g of divinylmercury was added, bringing the total to 85 g (0.3 mole). Rapid stirring was continued, and more aluminum metal was added in portions of 3–5 g (granules) to make sure that a fresh metal surface was always present. Addition was stopped when no more aluminum amalgam was formed. This took about 4 hrs and 80 g of aluminum. The solution was allowed to settle and was then filtered, and the solvent was distilled off in vacuo. Since trivinylaluminum is very sensitive to air and moisture, these manipulations were carried out under an atmosphere of dry nitrogen. After the pentane had been removed a light yellow, viscous liquid stayed behind. The compound will slowly polymerize at room temperature and cannot be heated to a high temperature. However, it moves through the vacuum system when pumped on. The boiling point of the freshly prepared material is 55 °C (1 mmHg). For analytical purposes, the THF addition compound was prepared. Its infrared spectrum was identical with that of the $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{CH}_2)_4$ prepared by the Grignard method. The yield $[(\text{CH}_2=\text{CH})_3\text{Al}]$ was 18.7 g (76.5%).

Hydrolysis was carried out on pure samples; in a typical run 0.2625 g of $(\text{CH}_2=\text{CH})_3\text{Al}$ yielded 161.2 ml (99.51%) of ethylene at STP.

Trivinylaluminum-Trimethylamine

From $\text{AlH}_3:\text{N}(\text{CH}_3)_3$ and $(\text{CH}_2=\text{CH})_2\text{Hg}$:

To 8.9 g (0.1 mole) of $\text{AlH}_3:\text{N}(\text{CH}_3)_3$ in 150 ml of ether was added 44.5 g (0.175 mole) of $(\text{CH}_2=\text{CH})_2\text{Hg}$, and the mixture was refluxed for 16 hrs while stirring. During this time 0.148 mole of hydrogen (calcd. 0.15 mole) evolved and was pumped off and measured. The solution was then filtered through a fine sintered glass disc and the ether removed. A slightly yellow, clear liquid stayed behind which distilled at 45 °C (10⁻³ mmHg). The compound melts at -94 °C.

Anal. calcd. for $\text{C}_9\text{H}_{18}\text{NAl}$:

C 64.63 H 10.85 N 8.38 Al 16.13.

Found: C 64.47 H 11.38 N 8.25 Al 15.75.

The infrared spectrum of this compound was identical with that of the compound prepared from $(\text{CH}_2=\text{CH})_3\text{Al}$ and $(\text{CH}_3)_3\text{N}$. Also, $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$ is formed when $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{CH}_2)_4$ or

¹⁹ Microanalysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

$(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{C}_2\text{H}_5)_2$ is treated with trimethylamine.

From $\text{AlCl}_3:\text{N}(\text{CH}_3)_3$ and $\text{CH}_2=\text{CHNa}$:

In 200 ml of dry ether was dissolved 19.2 g (0.1 mole) of $\text{AlCl}_3:\text{N}(\text{CH}_3)_3$ which was resublimed before use; the mixture was then slowly dropped into 16.5 g (0.33 mole) of vinylsodium⁸ in ether while cooling and stirring. The mixture is then refluxed for several hours and filtered from the NaCl , and the ether is removed in vacuum. The trivinylaluminum-trimethylamine may then be distilled *in vacuo*. Its infrared spectrum and elemental analysis are identical with those of $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$ synthesized by other methods.

Trivinylaluminum-Etherate

To 15.0 g of $(\text{CH}_2=\text{CH})_3\text{Al}$ in pentane was added 30 ml of ether distilled from LiAlH_4 . The mixture was stirred for 1 hr, and then the excess ether and pentane removed. Trivinylaluminum-etherate distills as a water-clear liquid at 60°C (1 mmHg). Its melting point is -54.5°C .

Anal. calcd. for $\text{C}_{10}\text{H}_{19}\text{OAl}$:

C 65.90 H 10.50 Al 14.80.

Found: C 64.80 H 11.11 Al 15.44.

Trivinylaluminum-Pyridine

This adduct was prepared by condensing 2.0 g (0.025 mole) of pyridine onto 3.3 g (0.018 mole) of $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{CH}_2)_4$. As the reaction mixture warmed from liquid nitrogen temperature to room temperature, a smooth reaction took place which resulted in the formation of a white, flaky solid. After the excess pyridine and the tetrahydrofurane which had been liberated were pumped away, the product was found to sublime readily at a bath temperature of about 50°C (10^{-3} mmHg). The melting point of the purified material was 43.8°C .

Anal. calcd. for $\text{C}_{11}\text{H}_{14}\text{NAl}$:

C 70.57 H 7.54 N 7.48 Al 14.41.

Found: C 70.48 H 7.89 N 7.90 Al 14.90.

Molecular Weight Determination of $(\text{CH}_2=\text{CH})_3\text{Al}$ and Some Derivatives

The cryoscopic molecular weight determination of $(\text{CH}_2=\text{CH})_3\text{Al}$ proved to be more involved than had been anticipated. In addition to the usual precautions which had to be taken to exclude oxygen and moisture, the tendency of the compound to polymerize made it difficult to obtain a satisfactory sample. In order not to lose any time between preparation of the $(\text{CH}_2=\text{CH})_3\text{Al}$ and the determination of the freezing point and to prevent polymerization as much as possible, the following method was used: The preparation of $(\text{CH}_2=\text{CH})_3\text{Al}$ was carried out in cyclohexane, the solvent used for the molecular weight determination, and the whole apparatus was placed in an inert atmosphere chamber. As soon as all of the divinylmercury used in the preparation had reacted, the solution was

filtered to free it from unreacted aluminum metal and amalgam sludge. An aliquot part of the cyclohexane solution was then carefully measured with a burette and introduced into the molecular weight apparatus. After the freezing point depression had been measured, the solution was hydrolyzed and the aluminum content was determined gravimetrically by converting to Al_2O_3 . From the aluminum the quantity of $(\text{CH}_2=\text{CH})_3\text{Al}$ could be calculated, and from this the molecular weight could be determined. This method was carefully tested with $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{C}_2\text{H}_5)_2$ and $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$, and excellent results were obtained.

a. $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{C}_2\text{H}_5)_2$

For $(\text{CH}_2=\text{CH})_3\text{Al}:\text{O}(\text{C}_2\text{H}_5)_2$ calcd: Al, 14.80.

Found: Al, 14.52. Molecular weight calcd: 182.2.

Found: 181.5.

b. $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$

For $(\text{CH}_2=\text{CH})_3\text{Al}:\text{N}(\text{CH}_3)_3$ calcd: Al, 16.13.

Found: Al, 15.80. Molecular weight calcd: 167.20.

Found: 169.21.

c. $(\text{CH}_2=\text{CH})_3\text{Al}$

Sample (a)

Molecular weight of $[(\text{CH}_2=\text{CH})_3\text{Al}]_3$ calcd: 324.36. Found: 284.52.

Sample (b) (Taken one hour after sample (a))

Molecular weight for $[(\text{CH}_2=\text{CH})_3\text{Al}]_5$ calcd: 540.00. Found: 582.80.

No lower molecular weight value than 284.50 was found in any run.

Vinylaluminum-Hydride-Trimethylamine

In a 250 ml, 3-neck, round bottom flask equipped with a stirrer, reflux condenser, dropping funnel, and gas inlet tube was placed 17.8 g (0.2 mole) of $\text{AlH}_3:\text{N}(\text{CH}_3)_3$ freshly resublimed. One hundred ml of dry ether was added to dissolve the hydride while the apparatus was flushed with dry nitrogen. The amount of divinylmercury required was 25.4 g (0.1 mole). However, only 24.5 g was used, allowing for slight hydride decomposition. The dropwise addition of the weighed amount of $(\text{CH}_2=\text{CH})_2\text{Hg}$ in 35 ml of ether took about 1 hr. Evolution of hydrogen started immediately. The mixture was then refluxed overnight. After this, no odor of $(\text{CH}_2=\text{CH})_2\text{Hg}$ could be detected, and no more H_2 was formed. During the time of reaction, 0.097 mole of hydrogen (calcd. 0.1 mole) evolved and was pumped off and measured. The solution was then filtered several times through a fine sintered glass disc until clear. The ether was then removed in *vacuo*, and the mixture was pumped on for several hours. A white solid stayed behind, which recrystallized from ether melts at $99-100^\circ\text{C}$ with decomposition.

Anal. calcd. for $\text{C}_5\text{H}_{14}\text{NAl}$:

C 52.16 H 12.25 N 12.16 Al 23.43.

Found: C 52.31 H 11.98 N 12.25 Al 23.30.

Lithium-Aluminum-Tetravinylate

On 7.6 g (0.02 mole) LiAlH_4 (100 mesh, crystalline) in 100ml of dry ether was condensed 11.4 g (0.045 mole) of $(\text{CH}_2=\text{CH})_2\text{Hg}$. The reaction mixture was allowed to warm slowly to room temperature and stirred for 16 hrs (overnight) and then filtered in an N_2 atmosphere. During this time 0.0399 mole of hydrogen (calcd. 0.04 mole) was evolved, pumped off and measured. The ether was then removed *in vacuo* and the remaining soluble, fluffy precipitate extracted with several portions of benzene. Upon cooling a white material precipitates which is filtered off and dried in vacuum. Recrystallized from benzene, the very fine white needles decompose at 180°C .

Anal. calcd. for $\text{LiAlC}_8\text{H}_{12}$:

Li 4.88 Al 18.98 C 67.61 H 8.51.

Found: Li 4.90 Al 19.30 C 67.30 H 8.20.

The material is pyrophoric and burns in air with a sparkling flame.

In addition to infrared spectra, elemental analysis and molecular weight determinations, structural proof for the vinylaluminum compounds was provided by N.M.R. spectra taken at the Naval Ordnance Test Station, China Lake, California, for which we would like to extend our gratitude to Messrs. D. W. MOORE and J. A. HAPPE²⁰. The authors also wish to thank Dr. CHARLES P. HABER for his helpful suggestions during the course of this work.

²⁰ D. W. MOORE and J. A. HAPPE, J. physic. Chem. **65**, 224 [1961].

Die chemische Natur des Wehrsekretes von *Pseudophonus pubescens* und *Ps. griseus*

VIII. Mitteilung über Insektenabwehrstoffe*

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Bei der Käfergattung *Pseudophonus* konnte als Abwehrstoff Ameisensäure nachgewiesen werden. Die Käfer speichern etwa 2 mg der 70- bis 75-proz. Säure in jeder der paarig angeordneten Pygidialblasen.

Allgemeines

In Deutschland kommen lediglich zwei Vertreter der Gattung *Pseudophonus* vor, es sind dies *Pseudophonus pubescens* Müll. und *Ps. griseus* Panz¹. Vom April bis August sind diese auf Feldern und Fluren in großer Zahl aufzufinden. Auch unter Steinen an den Rändern sandiger Feldwege wird man sie häufig antreffen. Tagsüber suchen sie unter Erdschollen und Grasnarben Schutz vor dem Licht, wobei sie stets darauf bedacht sind, einen feuchten Schlupfwinkel ausfindig zu machen.

Der Käfer wird man leicht habhaft, wenn man nach einem längeren Regen am Rande von Getreidefeldern Schollen und die beim Pflügen losgerissenen Grasnarben umwendet. Vielfach leben *Ps. pubescens* (14–16 mm) und *Ps. griseus* (9–11 mm) gesellschaftlich zusammen. Zur Haltung wurden Terrarien mit Ackererde gefüllt und einige flache Steine dienten als Unterschlupf. Als Futter eigneten sich kleine

Rindfleischstückchen sowie zerstampfte Schnecken und Regenwürmer.

Die Pygidialblasen

Wie bei anderen Laufkäferarten befinden sich an beiden Seiten des Afters die Ausführungsgänge der Pygidialblasen. Diese sind hell und durchsichtig, ihre Wand ist von Muskelfasern durchzogen, welche eine Kontraktion des Reservoirs und damit ein Entleeren desselben ermöglichen. Die zur Längsachse des Käfers symmetrisch angeordneten beiden Blasen erreichen eine Länge von 1,5–2 mm, sobald sie mit Sekret prall angefüllt sind. Das Sekret selbst stellt eine wasserhelle, relativ flüchtige Flüssigkeit dar. Bei Bedrohung durch einen Feind wird es bis zu einer Entfernung von etwa 20 cm in feinen Tröpfchen gezielt ausgespritzt.

Analyse des Abwehrstoffes

Vorproben

Der Geruch des Abwehrstoffes ist scharf und stechend. Die Nasenschleimhaut erleidet eine Verätzung

* II. Mitteilung s. Z. Naturforsch., im Druck.

¹ E. REITTER, Fauna Germanica, die Käfer des Deutschen Reiches, K. G. Lutz Verlag, Stuttgart 1908, Bd. I, S. 170.