LEAD

ANNUAL SURVEY COVERING THE YEAR 1971*

L. C. Willemsens
Organisch Chemisch Instituut TNO, Utrecht (The Netherlands)

Reviews

The following aspects of organolead chemistry have been reviewed: alkali metal and magnesium derivatives [1]; compounds containing a lead-transition element bond [2]; derivatives of keto enols [3]; sulphinate complexes [4]; preparation via aryldiazonium and diaryliodonium salts [5]; heterocyclic compounds containing lead as a hetero atom [6]; vibrational absorptions due to lead-metal bonds [7]; biologically active organolead polymers [8]; effects of leaded gasolines on exhaust emission [9]. A review on recent literature has appeared [10].

Preparations

Seyferth and Andrews [11] prepared halomethyl-metal compounds via the Simmons-Smith reagent, e. g.:

$$Zn + CH_2I_2 \longrightarrow IZnCH_2I \xrightarrow{Ph_3PbCl} Ph_3PbCH_2I$$

Jensen and Davis [12] studied optically active organometallic compounds, e.

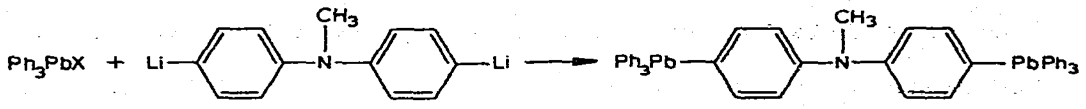
$$Ph_3PbNa + (S)\text{-}(+)\text{-}s\text{-}BuBr \xrightarrow[67.5\%]{S_N2} Ph_3Pb\text{-}s\text{-}Bu\text{-}(-)\text{-}(R)$$

inversion

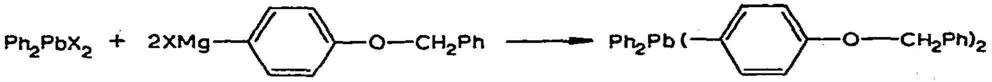
Laliberte et al. carried out the following preparations:

---

* The 1972 literature which has come to my attention before June 1st, 1972 has been included. Some of the 1971 literature has already been dealt with in the 1970 annual survey.

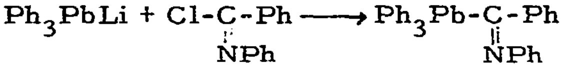


57% (ref. [13])



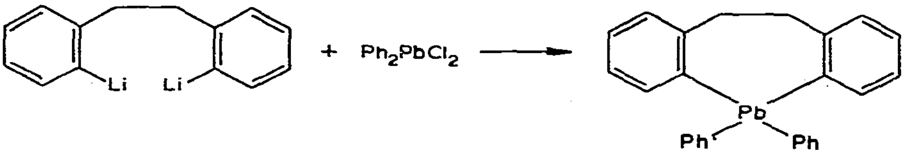
52% (ref. [14])

Jappy and Preston [15] synthesized α-iminoalkyl-metal derivatives from e. g. triphenylplumbyllithium:

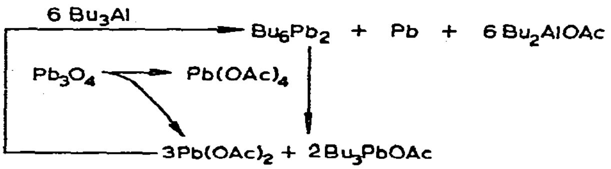


$$\mathrm{Ph_3PbLi + Cl\text{-}\underset{\underset{NPh}{\parallel}}{C}\text{-}Ph \longrightarrow Ph_3Pb\text{-}\underset{\underset{NPh}{\parallel}}{C}\text{-}Ph}$$

Heterocyclic compounds with a metal as the hetero atom were prepared by Corey et al. [16]:



The following reaction cycle has been described in a patent [17] as an economic way to produce tributyllead acetate:



Pant and Noltes [18] found the following convenient method for the preparation of benzotriazolyl-lead derivatives:

The order of cleavage of groups in mixed-organolead compounds is:

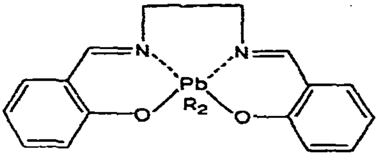
$CH_2\text{-}CH{=}CH_2,\ C{\equiv}C\text{-}CMe_3 < Ph < Alkyl$

Bertazzi et al. [19] prepared organolead (iso)thiocyanates. From IR studies it was concluded that these compounds are actually isothiocyanates, R_3PbNCS. There is evidence for a polymeric nature in the solid state through NCS bridging.

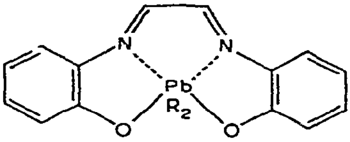
Di Bianca et al. [20] studied diorganolead complexes with ONNO tetradentate ligands:

$$R_2PbX_2 + H_2L \xrightarrow{NaOMe} R_2PbL$$

From IR, UV and NMR spectra the following structures were concluded:



R=Me, Et, Ph



Pudovik et al. [21] prepared organolead dithiophosphates:

$$Et_4Pb + HSP(S)(OR)_2 \longrightarrow Et_3Pb\text{-}SP(S)(OR)_2 \longrightarrow Et_2Pb[SP(S)(OR)_2]_2$$

R = Me, Pr, i-Pr, Bu

Diethyl- and dipropyllead oxide were prepared by Alexandrov and Sheyanov [22] through ozonization of tetraethyllead.

Puddephatt and Thistlethwaite [23] prepared so far unknown dimethyllead dialkoxides by cleavage of dimethyldi-1-propynyllead with alcohols:

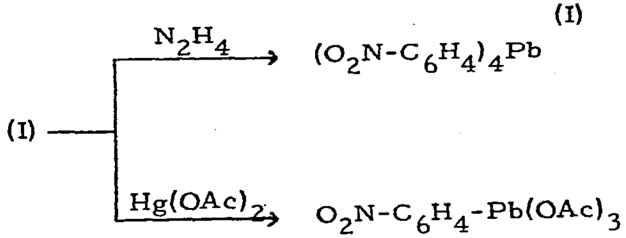
$$Me_2Pb(\text{-}C{\equiv}CMe)_2 + 2\ ROH \longrightarrow Me_2Pb(OR)_2 + 2\ HC{\equiv}CMe$$

A patent [24] describes the preparation of phenyllead triacetate in 77% yield in one step from hexaphenyldilead. The reaction was carried out in acetic acid at 40-70°, and was catalyzed by mercuric salts (5-20 mole%):

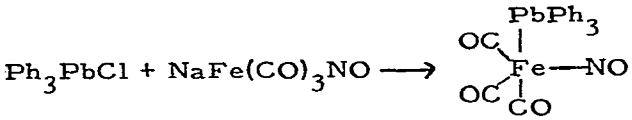
$$Ph_6Pb_2 + 5\ Pb(OAc)_4 \longrightarrow 6\ PhPb(OAc)_3 + Pb(OAc)_2$$

Huber and Kunze [25] reported on the preparation of nitrophenyllead compounds:

$$Ph_2Pb(NO_3)_2 \xrightarrow{\text{nitration}} \underset{(I)}{(O_2N\text{-}C_6H_4)_2Pb(NO_3)_2}$$



Cleland et al. [26] prepared tricarbonyl nitrosyl iron derivatives of germanium, tin and lead:



The structure was concluded from IR data.

According to Haupt and Huber [27] diphenyllead dihalide gives with triphenyl phosphine oxide two kinds of complexes, trigonal bipyramidal $Ph_2PbX_2 \cdot Ph_3PO$ and octahedral $Ph_2PbX_2 \cdot 2\ Ph_3PO$.

Reactions

Gaseous tetramethyllead decomposes at temperatures between 240 and 370° at a pressure lower than 25 mm with formation of methane and ethane [28]. Addition of toluene increases the CH_4/C_2H_6 ratio.

The decomposition rate of tetramethyllead in dilute mixtures with argon, argon + oxygen, and air at 890-1060°K behind incident shock waves was found to be first-order [29]; $\log k = 4.25 \times 10^3 \times T$. Lead-containing particles formed rapidly:

$$Me_4Pb \longrightarrow Pb(g) \longrightarrow Pb(s) \longrightarrow PbO(s)$$

The results support the theory that PbO smoke inhibits spontaneous ignition in fuels.

A layer of tetraethyllead condensed on glass decomposes when irradiated with UV light of 254 nm to give a lead film and gaseous hydrocarbons (C_2/C_4 ratio 3.6) [30].

A reaction scheme has been suggested [31] that fits the results of the reaction of tetramethyllead with oxygen. The major products in the early stage were carbon dioxide and hydrogen. No Me_3PbCH_2 radicals are involved.

Ozonolysis of Et_4Pb in CCl_4 at room temperature is a bimolecular process; E_a(Pb) 7200 cal/mole [32].

Tetraphenyllead reacts with allylpalladium chloride dimer in methylene chloride at room temp. with formation of lead chloride (45%), benzene (3%), biphenyl (15%), allylbenzene (10%), 1,5-hexadiene (14%). A mechanism based on catalyzed exchange of phenyl groups and chlorine atoms has been proposed [33].

A slow exchange of alkyl groups between tetramethyllead and trimethylaluminium has been observed [34]. Under basic conditions this exchange is suppressed.

Hexaphenyldilead is cleaved by mercuric salts with formation of Ph_3PbX, Ph_2PbX_2, PbX_2, Hg, PhHgX. A mechanism has been proposed [35] in which the first step is rate-controlling:

$$\begin{tikzcd}[column sep=small] Ph_6Pb_2 + HgX_2 \arrow[r] & {[Ph_5Pb_2X]} \arrow[d] & + PhHgX \\ & \text{other products} & \end{tikzcd}$$

Dimethyllead dihalide [36] decomposes in aqueous solutions in a first-order reaction according to:

$$2\ Me_2PbX_2 \longrightarrow Me_3PbX + PbX_2 + MeX$$

Triethyllead peracetate in chlorobenzene decomposes in two ways [37]:

$$\begin{tikzcd} & Et_3PbOAc + O \\ Et_3Pb\text{-}O\text{-}OAc \arrow[ur] \arrow[dr] & \\ & Et_2Pb(OEt)(OAc) \end{tikzcd}$$

In methanol only the first route occurs.

Physico-chemical investigations

Pilloni and Magno [38] continued their study of the hydrolytic stability of organolead salts with the determination of the stability of (mononuclear) organolead(IV) halides complexes in 1 M aq. $HClO_4$ at 25°.

Triorganolead salts can be determined in buffers at pH ≈ 7 using polarography. A linear relationship exists between the first wave diffusion current and concentration [39].

A paper dealing with conformational analysis of tetraphenyllead has appeared [40].

The crystal parameters have been determined for Me_3PbCN (orthorhombic, Cmcm, a 9.64, b 12.01, c 6.27 Å) [41] and for $Me_2Pb(CN)_2$ (Fmm 2, a 9.02, b 8.37, c 8.88 Å, Z 4, d 2.77) [42]. The ligands in $Me_2Pb(CN)_2$ are nearly octahedrally arranged around the lead atom.

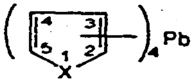
Vapour-state thermodynamic properties have been calculated for tetraethyllead. A molecular-vibrational analysis was used to estimate the unobserved C–Pb–C bending fundamentals, and vapour pressure data were used to estimate the enthalpy and entropy of vaporization [43]

The NMR spectra of tetrafurylleads and tetrathienylleads have been reported [44, 45] (see Table 1)

The $J(^{13}C-^{1}H)$ and $J(^{207}Pb-C-^{1}H)$ coupling constants of bis(acetylacetonato)dimethyllead in various solvents have been determined [46]. The couplings were found to increase with increasing donor strength of the solvent, e.g.:

	$J(^{13}C-H)$	$J(^{207}Pb-CH_3)$	$\delta(PbCH_3)$	$\delta(CCH_3)$
$CHCl_3$	144.6	154.7	2.05	1.92
HMPT	153.6	182.7	1.79	1.77

TABLE 1



(X=O,S)

	2-Furyl	2-Thienyl	3-Furyl	3-Thienyl
Chemical shifts, δ (TMS = 0)				
2-H			7.41	7.50
3-H	6.80	7.43		
4-H	6.54	7.32	6.53	7.29
5-H	7.77	7.71	7.66	7.54
^{207}Pb-^{1}H coupling constants (Hz)				
2-H			16.1	54.2
3-H	9.8	58.7		
4-H	15.8	18.1	24.9	25.3
5-H	18.3	30.3	14.9	15.7

The ^{19}F NMR spectrum of monofluorophenyllead compounds has been studied [47].

Internuclear double resonance (INDOR) spectra of tetramethyllead and tetraethyllead have been reported [48].

From the mass spectra of tetramethyllead and hexamethyldilead thermochemical data have been derived [49], e.g. E(Me-Pb) in Me_4Pb is 32.9 kcal/mole, E(Pb-Pb) in Me_6Pb_2 33.3 kcal/mole.

The mass spectrum of dicyclopentadienyllead shows as the main peaks: $CpPb^+$ (100.0) and Pb^+ (80.3) [50].

Electron diffraction of tetramethyllead gave the following structural parameters [51]: r_g(Pb-C) 2.238, r_g(Pb---H) 2.72, r_g(C-H) 1.08 and r_g(C---C) 3.66 Å.

Toxicology

The LD_{50} value of tetraethyllead was redetermined [52]: 12.6 to 15.9 mg/kg of rat for a single oral dose.

The threshold of the neuromuscular excitation in mice decreased from 17.5 V to 12.5 V after exposure for two hours a day for 4 months to 0.001 mg tetraethyllead per litre of air [53].

Homogenates of rat and rabbit tissues dealkylate tetraethyllead to Et_3Pb^+. The order of activity is: liver > kidney > brain [54]. Similarly liver microsomes dealkylate tetraethyllead [55]. From the formation of 1-butene it was concluded that hydroxylation at the 1-position of the organic moiety is involved.

The fate of triphenyllead acetate in rats has been studied with triphenyllead acetate labeled with ^{14}C in the phenyl groups [56]. Within 7 days 25% of the phenyl groups was found in the urine, 29% in the faeces and 20% (as benzene) in the expired air.

Applications

The excellent antifouling properties of triphenyllead acetate have been confirmed [57].

Tributyllead acetate is effective as a wood preservative [58]. Complete protection against three fungi was obtained at 2.6 kg lead compound per m^3 of wood.

Triphenyllead acetate inhibits the growth of various strains of yeasts, molds and bacteria at a concentration of 2-25 ppm [59]. From tracer studies it was concluded that the lead compound primarily interferes with the biosynthesis of DNA and RNA.

Triorganolead salts suppress the growth of aquatic organisms at a concentration of less than 1 ppm [60].

BAL (1, 2-dithioglycerol) is an effective counterpoison of the anthelmintic dibutyllead diacetate [61].

REFERENCES

1 D. D. Davis and C. E. Gray, Organometal. Chem. Rev., Sect. A, 6 (1970) 283-318; Chem. Abstr., 75 (1971) 63857d

2 F. Glockling and S. R. Stobart, Inorg. Chem. Ser. One, 6 (1972) 63-120; Chem. Abstr.,76 (1972) 99725u

3 Yu. I. Baukov en I. F. Lutsenko, Organometal. Chem. Rev., Sect. A, 6 (1970) 355-445; Chem. Abstr.,75 (1971) 63855b

4 G. Vitzthum and E. Lindner, Angew. Chem., 83 (1971) 315-27

5 O. A. Ptitsyna, Probl. Org. Khim., (1970) 73-85; Chem. Abstr.,74 (1971) 125754h

6 C. H. Yoder and J. J. Zuckerman, Prep. Inorg. React.,6 (1971) 81-155; Chem. Abstr.,75 (1971) 118355w

7 E. Maslowsky Jr., Chem. Rev.,71 (1971) 507-24;

8 D. A. Kochkin, I. S. Novoderezhkina, P. I. Zubov and N. A. Voronkov, Kinet. Mech. Polyreactions, Int. Symp. Macromol. Chem. Prepr., 1 (1969) 175-9; Chem. Abstr.,75 (1971) 78223t

9 Coordination Research Council, Inc., New York,1970 101p.; Chem. Abstr.,75 (1971) 67215r

10 A. J. Bloodworth, MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.; Inorg. Chem. Ser. One 4 (1972) 275-354

11 D. Seyferth and S. B. Andrews, J. Organometal. Chem., 30 (1971) 151-66

12 F. R. Jensen and D. D. Davis, J. Amer. Chem. Soc.,93 (1971) 4047-8; Chem. Abstr.,75 (1971) 110385k

13 B.R. Laliberte and S.A. Leone, J. Organometal. Chem., 37 (1972) 209-15; Chem. Abstr., 76 (1972) 133814n

14 W. Davidsohn, B.R. Laliberte, C.M. Goddard and M.C. Henry, J. Organometal. Chem., 36 (1972) 283-91;

15 J. Jappy and P.N. Preston, Inorg. Nucl. Chem. Lett., 7 (1971) 181-5; Chem. Abstr., 75 (1971) 20547k

16 J.Y. Corey, M. Dueber and M. Malaidza, J. Organometal. Chem., 36 (1972) 49-60; Chem. Abstr., 76 (1972) 153875h

17 M. Buschhoff (Schering A.G.), Ger. Offen 2,032,426; Chem. Abstr., 76 (1972) 59756y; Ger. Offen 2,032,299; Chem. Abstr., 76 (1972) 59754w

18 B.C. Pant and J.G. Noltes, J. Organometal. Chem., 36 (1972) 293-6

19 N. Bertazzi, G. Alonzo, A. Silvestri and G. Consiglio, J. Organometal. Chem., 37 (1972) 281-4; Chem. Abstr., 76 (1972) 153864d

20 F. di Bianca, E. Rivarola, G.C. Stocco and R. Barbieri, Z. Anorg. Allg. Chem., 387 (1972) 126-33

21 A.N. Pudovik, R.A. Cherkasov and I.V. Shergina, Zh. Obshch. Khim., 41 (1971) 1472-6; Chem. Abstr., 75 (1971) 140947n; U.S.S.R. 293,814; Chem. Abstr., 75 (1971) 77035w

22 Yu.A. Aleksandrov and N.G. Sheyanov, Zh. Obshch. Khim., 40 (1970) 1907; Chem. Abstr., 74 (1971) 125805a

23 R.J. Puddephatt and G.H. Thistlethwaite, J. Chem. Soc., Dalton Trans., (1972) 570-2; Chem. Abstr., 76 (1972) 85892j

24 M. Buschhoff and A. Bokranz (Schering A.G.), Ger. Offen 2,032,305; Chem. Abstr., 76 (1972) 85922u

25 F. Huber and E. Kunze, Angew. Chem., 73 (1971) 916

26 A.J. Cleland, S.A. Fieldhouse, B.H. Freeland, C.D.M. Mann and R.J. O'Brien, J. Chem. Soc. A, (1971) 736-8

27 H.J. Haupt and F. Huber, J. Organometal. Chem., 33 (1971) 175-80

28 D.E. Hoare, T.-M. Li and A.D. Walsh, Symp. (Int.) Combust [Proc.], 12th (1969) 357; Chem. Abstr., 74 (1971) 111395e

29 J. B. Homer and I. R. Hurle, Proc. Roy. Soc., Ser. A, 327 (1972) 61-79; Chem. Abstr., 76 (1972) 61534t

30 D. L. Perry and M. W. Roberts, J. Chem. Soc., Chem. Commun., (1972) 147; Chem. Abstr., 76 (1972) 106400q

31 D. E. Hoare, A. D. Walsh and Ting-man Li, Symp. (Int.) Combust [Proc.], 13th, 1970 (publ. 1971) 461-9; Chem. Abstr., 76 (1972) 14668e

32 Yu. A. Aleksandrov, B. I. Tarunin and V. A. Shushunov, Kinet. Katal., 12 (1971) 898-902; Chem. Abstr., 75 (1971) 151024k

33 G. A. Domrachev, K. G. Shal'nova and V. A. Varyukhin, Zh. Obshch. Khim., 41 (1971) 1924-5; Chem. Abstr., 76 (1972) 24408j

34 M. Boleslawski, S. Pasynkiewicz and K. Jaworski, J. Organometal. Chem 30 (1971) 199-209; Chem. Abstr., 75 (1971) 76968r

35 V. G. K. Das, D. A. Moyes and P. R. Wells, J. Organometal. Chem., 33 (1971) 31-40; Chem. Abstr., 76 (1972) 99781j

36 F. Huber, J. Gmehling, H. J. Haupt and H. Lindemann, Angew. Chem., 83 (1971) 909-10

37 V. D. Mal'kov, V. P. Maslennikov, V. A. Shushunov and V. I. Buzulukov, Tr. Khim. Khim. Tekhnol., (1971) 101-4; Chem. Abstr., 75 (1971) 75853n

38 G. Pilloni and F. Magno, Inorg. Chim. Acta 5 (1971) 30-2; Chem. Abstr., 75 (1971) 41100z

39 D. A. Kochkin, T. L. Shkorbatova, L. I. Ryzhova and G. E. El'khanov, Zh. Obshch. Khim., 41 (1971) 75-80; Chem. Abstr., 75 (1971) 14222j

40 N. A. Ahmed, A. I. Kitaigorodskii and K. V. Mirskaya, Acta Crystallogr., Sect. B, 27 (1971) 867-70; Chem. Abstr., 75 (1971) 54790z

41 Y. M. Chow and D. Britton, Acta Crystallogr., Sect. B, 27 (1971) 856-7; Chem. Abstr., 75 (1971) 54784a

42 J. Konnert, D. Britton and Y. M. Chow, Acta Crystallogr., Sect. B, 28 (1972) 180-7; Chem. Abstr., 76 (1972) 51272s

43 D. W. Scott, J. Chem. Thermodyn., 4 (1972) 99-104; Chem. Abstr., 76 (1972) 77414q

44 A. P. Ebdon, T. N. Huckerby and F. G. Thorpe, Tetrahedron Lett., (1971) 2921-4; Chem. Abstr.,73 (1971) 114624k

45 G. Barbieri and F. Taddei, J. Chem. Soc., Perkin Trans.,2 (1972) 262-5

46 M. Aritomi, Y. Kawasaki and R. Okawara, Inorg. Nucl. Chem. Lett., 8 (1972) 69-71

47 A. N. Nesmeyanov, D. N. Kravtsov, B. A. Kvasov, E. I. Fedin and T. S. Khazanova, Dokl. Akad. Nauk SSSR, 199 (1971) 1078-81; Chem. Abstr.,75 (1971) 139926y

48 P. J. Banney, D. C. McWilliam and P. R. Wells, J. Magn. Resonance, 2 (1970) 235-42; Chem. Abstr.,74 (1971) 118125a

49 M. F. Lappert, J. B. Pedley, J. Simpson and T. R. Spalding, J. Organometal. Chem.,29 (1971) 195-208; Chem. Abstr.,75 (1971) 55152e

50 V. Mikulaj, Z. Naturforsch. A, 26 (1971) 1104; Chem. Abstr.,75 (1971) 81580n

51 T. Oyamada, T. Iijima and M. Kimura, Bull. Chem. Soc. Jap.,44 (1971) 2638-42; Chem. Abstr.,76 (1972) 7585x

52 T. Schroeder, D. D. Avery and H. A. Cross, Experientia, 28 (1972) 425-6

53 I. Ya. Nagaev, G. I. Oksengendler and V. A. Rzhevkin, Gig. Tr. Prof. Zabol.,15 (1971) 48-9; Chem. Abstr.,75 (1971) 59546j

54 W. Bolanowska and J. M. Wisniewska-Knypl, Biochem. Pharmacol.,20 (1971) 2108-10; Chem. Abstr.,76 (1972) 81883j

55 J. E. Casida, E. C. Kimmel, B. Holm and G. Widmark, Acta Chem. Scand., 25 (1971) 1497-9; Chem. Abstr.,76 (1972) 42199w

56 B. Williams, L. G. Dring and R. T. Williams, Biochem. J.,127 (1972) 24P-25P

57 J. Lorenz, 2nd Int. Biodeterioration Symp., Lunteren (Holland) 13-18 sep. 1971

58 E. W. B. Da Costa and L. D. Osborne, Holzforschung, 25 (1971) 119; Chem. Abstr.,75 (1971) 128763s

59 H. Kourai, K. Takeichi, M. Okazaki, T. Enatsu and I. Shibasaki, Hakko Kogaku Zasshi, 49 (1971) 47-52; Chem. Abstr., 74 (1971) 73224p

60 N. S. Stroganov, V. G. Khobot'ev and L. V. Kolosova, Vop. Vod. Toksikol. (1970) 66-74; Chem. Abstr., 74 (1971) 121801y

61 G. Gras, H. Giono, L. C. Willemsens, G. J. M. van der Kerk and G. M. van der Want, C. R. Acad. Sci., Ser. D, 272 (1971) 2626-9