LEAD

ANNUAL SURVEY COVERING THE YEAR 1972+

L. C. Willemsens

Organisch Chemisch Instituut TNO, Utrecht (The Netherlands)

Reviews

In the following reviews specific aspects of organolead chemistry have been dealt with: reactions with polyhalomethanes [1]; reactions with peroxides [2]; cyclopentadienyl derivatives [3].

Preparations

In a patent [4] the use of hexamethylphosphoric triamide (HMPT) as a solvent or as a catalyst is reported to be of advantage in the preparation of tetraethyllead from lead diacetate and triethylaluminium.

When equimolar amounts of trimethylaluminium and lead oxide were refluxed for 8 h in xylene, 26% of the methyl groups were transferred from aluminium to lead [5]. Not more than one methyl group of trimethylaluminium can be utilized.

Puddephatt and Thistlethwaite [6] prepared a series of alkynyl-lead compounds as follows:

$$\left.\begin{array}{l} R_3PbCl + LiC\equiv CR' \\ R_3PbOMe + H\text{-}C\equiv CR' \end{array}\right] \longrightarrow R_3Pb\text{-}C\equiv C\text{-}R'$$

From NMR spectra it was concluded that these compounds form weak adducts with Lewis bases.

+ The 1973 literature which has come to my attention before May 15, 1973 has been included. Some of the 1972 literature has already been dealt with in the 1971 annual survey.

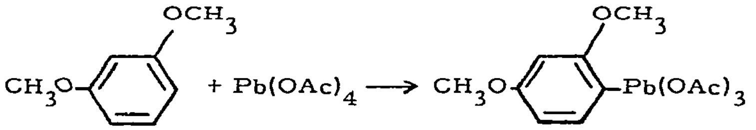
Juenge et al. [7] synthesized unsaturated organolead compounds via addition of organolead hydrides (prepared in situ) to acetylenic bonds, e.g.:

$$Et_3PbX + HC{\equiv}C\text{-}CH{=}CH_2 \xrightarrow[0^{\circ},\ THF]{LiAlH_4} Et_3Pb\text{-}CH{=}CH\text{-}CH{=}CH_2$$

Pant and Davidsohn [8] described a procedure for the preparation of triorganolead chlorides by cleavage of tetraorganoleads or hexaorganodileads with ammonium hexachloroplumbate

$$R_4Pb \text{ or } R_6Pb_2 \xrightarrow{(NH_4)_2PbCl_6} R_3PbCl$$

Certain aromatic ethers (with one alkoxy group, or better still with two alkoxy groups in 1, 3-position) can be directly plumbylated with lead tetraacetate to give aryllead triacetates [9], e.g.



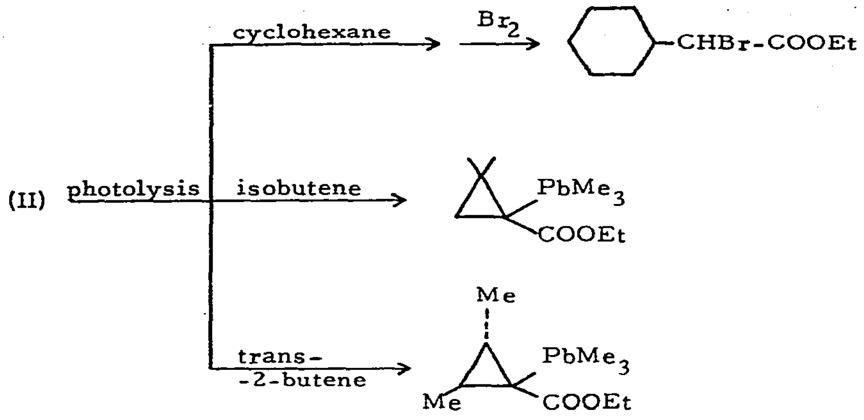
(I)

The reaction runs even more smoothly in the presence of halogenated acetic acids, e.g. chloroacetic acid, in this case producing aryllead tris(haloacetates) [10]. The NMR spectra of these compounds show very large coupling of the lead atom with the aromatic hydrogens, e.g. $J(^{207}Pb\text{-}H_{ortho})$ 386 Hz [11].

Similar compounds have been isolated from the reaction of lead tetrakis(trifluoroacetate) with halobenzenes or (p-halophenyl)metal compounds (metal = Si, Tl , Hg) [12].

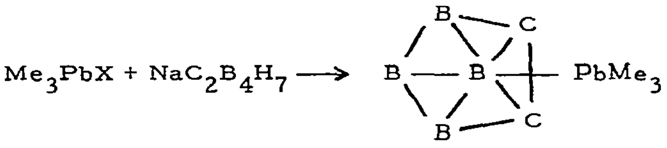
Schöllkopf et al. [13] studied properties of ethyl (trimethylmetallyl)-diazoacetates, e.g.:

$$Me_3Pb\text{-}N(SiMe_3)_2 + N_2CH\text{-}COOEt \longrightarrow Me_3Pb\text{-}CN_2\text{-}COOEt \qquad (II)$$



From the results it was concluded that the intermediate carbene $Me_3Pb\text{-}C\!:\!\text{-}COOEt$ reacts in the singlet state.

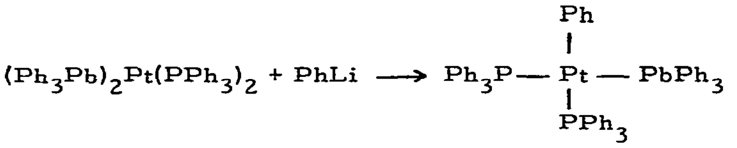
The product of the following reaction has been fully characterized by NMR and mass spectrometry [14]:



Hexaphenyldilead is cleaved by tetrakis(triphenylphosphine)palladium and -platinum [15]:

$$Ph_6Pb_2 + (Ph_3P)_4M \longrightarrow (Ph_3Pb)_2M(PPh_3)_2 + 2\ PPh_3 \qquad M = Pd,\ Pt$$

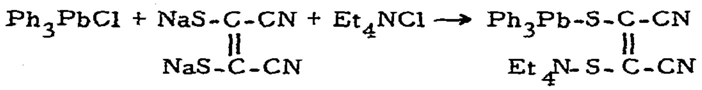
The product reacts with phenyllithium as follows:



$$(Ph_3Pb)_2Pt(PPh_3)_2 + PhLi \longrightarrow Ph_3P\text{—}\underset{\displaystyle PPh_3}{\overset{\displaystyle Ph}{Pt}}\text{—}PbPh_3 \qquad \text{(III)}$$

An X-ray structure determination showed (III) to be virtually planar (as drawn) with a Pb-Pt bond length of 2.698 Å and a Ph-Pt bond length of 2.055 Å. Hexamethyldilead reacts with $(Ph_3P)_4M$ to give directly $Me_3Pb\text{-}M(Me)(PPh_3)_2$.

The following metathetical reactions have been carried out:



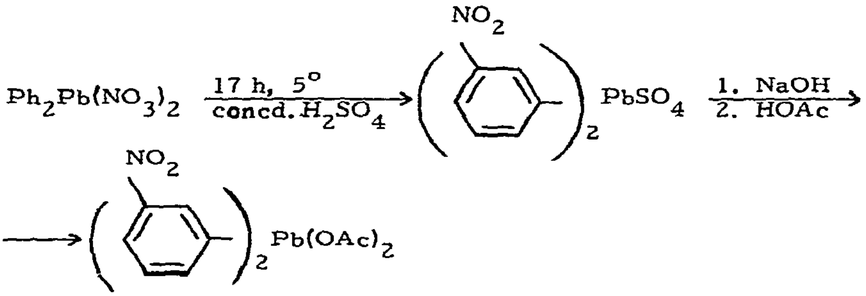
$$\begin{array}{c} Ph_3PbCl + NaS\text{-}C\text{-}CN \\ \| \\ NaS\text{-}C\text{-}CN \end{array} + Et_4NCl \longrightarrow \begin{array}{c} Ph_3Pb\text{-}S\text{-}C\text{-}CN \\ \| \\ Et_4N\text{-}S\text{-}C\text{-}CN \end{array}$$ [16]

$$Ar_2Pb(OAc)_2 + H_2SO_4 \longrightarrow Ar_2PbSO_4$$ [17]

$$Ar_2Pb(OAc)_2 + 2\ HNO_3 \xrightarrow{HOAc} Ar_2Pb(NO_3)_2$$ [18]

Ar = Ph, p-MeC_6H_4, 3,5-$Me_2C_6H_3$, p-$MeOC_6H_4$, m-$MeOC_6H_4$, p-$MeSC_6H_4$

The dinitrates undergo nitration in the m-position in concentrated sulphuric acid [16] e.g.:



The peracetate prepared according to:

$$Et_2Pb(OH)_2 + AcO_2H \xrightarrow{MeOH} Et_2Pb(O_2Ac)_2$$ [19]

decomposes with formation of $Et_2Pb(OAc)_2$, MeOAc, oxygen.

Except for the aryllead triacylates, $ArPb(OAcyl)_3$, and the polymeric arylplumbonic acids, ArPb(O)OH, compounds of the type $RPbX_3$ have so far not been characterized, owing to their instability. Huber et al. [20] now describe the preparation of some more stable complexes, e.g.:

$$PhPb(O)OH + HCl + Ph_4PCl \longrightarrow [Ph_4P]^+[PhPbCl_4]^-$$

With HF polymeric $PhPbF_3$ precipitates. Also complexes of phenyllead triacetate with DMSO and N-donor ligands are stable [21], e.g. $PhPb(OAc)_3 . H_2O . Py$.

Reactions

Tetraethyllead and tetramethyllead are produced on a large scale as anti-knock agents for gasolines. As a consequence they are relatively cheap and may therefore be attractive as starting materials. Thus, last year a patent [22] was published on the production of methyltin compounds starting from tetramethyllead and tin tetrachloride, e.g.:

$$2\ Me_4Pb + 3\ SnCl_4 \longrightarrow 3\ Me_2SnCl_2 + 2\ PbCl_2 + 2\ MeCl$$

$$4\ Me_4Pb + 3\ SnCl_4 \longrightarrow 3\ Me_4Sn + 4\ PbCl_2 + 4\ MeCl$$

The result mainly depends on the reactant ratio; 75% of the methyl groups attached to lead may be transferred to tin. The reaction is carried out in a concentrated solution in toluene or ethanol, initially for a few hours at ambient temperature, then after stripping off the solvent, at 130-140^o.

The flash photodecomposition of tetramethyllead has been monitored by time-resolved mass spectrometry [23]. The initial step is the cleavage of a methyl group. Gaseous products formed were hydrogen, methane, ethane, ethene, acetylene.

Williams [24] reinvestigated the reaction of tetraethyllead with dinitrogen tetraoxide and found the following reactions to occur:

$$R_4Pb + N_2O_4 \xrightarrow{\text{pentane}} R_3PbNO_3\downarrow + RNO$$

$$R_4Pb + 2\ N_2O_4 \xrightarrow{CHCl_3} R_2Pb(NO_3)_2 + 2\ RNO \longrightarrow [R_2Pb(RNO)_2][NO_3]_2$$

The reaction of tetraethyllead with acetic acid according to Clinton and Kochi [25] is strongly catalyzed by copper(I) species:

$$Et_4Pb + HOAc \xrightarrow{Cu^+} Et_3PbOAc + EtH$$

The intermediate step

$$Et_4Pb + CuOAc \longrightarrow Et_3PbOAc + EtCu$$

was considered as rate-limiting. The reaction is first-order in Et_4Pb and Cu^I. Copper(II) salts are first reduced to copper(I) with formation of ethylene [26]:

$$2\ Cu(OAc)_2 + Et_4Pb \longrightarrow 2\ CuOAc + Et_3PbOAc + H_2C{=}CH_2 + HOAc$$

Huber et al. [27] studied the decomposition of dimethyllead dichloride in the presence of various salts (e.g. LiCl, KCl):

$$2\ Me_2PbCl_2 \longrightarrow Me_3PbCl + MeCl + PbCl_2$$

The rate increased with increasing salt concentration. In the presence of pyridine $[MePy]^+[PbCl_3]^-$ is formed [28].

Dimeric $[R_2PbFe(CO)_4]_2$ undergoes facile and reversible homolysis [29] of metal-metal bonds by Lewis bases, e.g. pyridine, with formation of $R_2PbFe(CO)_4Py$.

Kinetics

Bertazzi et al. [30] measured the dependence of anion exchange distribution coefficients of Et_2PbCl_2 and Et_3PbCl on the acidity of the aqueous phase (total LiCl + HCl concentration 8.0 M). The results suggest retention of the species $Et_2PbCl_4^{2-}$ and $Et_3PbCl_3^{2-}$ in the resin phase.

The equilibrium constant of:

$$Me_2Pb(OBz)_2 + OP(NMe_2)_3 \rightleftarrows Me_2Pb(OBz)_2 \cdot OP(NMe_2)_3$$

in methylene chloride at room temperature has been determined [31]: $K = 36 \pm 4\ M^{-1}$.

The absolute rate constants for the reaction of hexaphenyldilead with tert-butylperoxy radicals in cumene at -70 and -100° is given by [32]:

$$\log (k_p) = (9.5 \pm 0.3) - (6000 \pm 250) / (2.303\ RT)$$

k in mol/sec, RT in cal/mole

Physical Chemistry

Abraham [33] studied solvent effects on the free energies of ions, pairs, non-electrolytes, and transition states in S_N and S_E reactions. Standard free energies of transfer from methanol to various other solvents for e.g. tetraethyllead are reported. A dissection of solvent influences on $\Delta G^{\ddagger}$ into initial-state and transition-state contributions has been accomplished for e.g. the reaction of tetraalkylleads with iodine.

The D[Me_3Pb-Me] value has been calculated [34] from the rate of the reaction

$$Me_4Pb \longrightarrow Me_3Pb^{\bullet} + Me^{\bullet}$$

during pyrolysis in a toluene carrier flow system at 671-753 K; $k_1 = 5.0 \times 10^{14} \times \exp(-49400/RT)\ sec^{-1}$; D[$Me_3Pb$-Me] = 35.7 kcal/mole.

The enthalpy of formation of tetraphenyllead has been determined [35] with a vacuum-jacketed rotating aneroid calorimeter;

$\Delta H^{o} = -(3115.6 \pm 3.6)$ kcal/mole

ΔH_f^{o} (Ph_4Pb, s) = 123.1 kcal/mole

The sublimation pressure, p, of a mixture of Ph_4Si and Ph_4Pb (completely miscible in the solid state) was measured [36] as a function of the composition in the range 453-488 K. Only Ph_4Si is volatile at these temperatures; $\ln p = A - BT^{-1}$.

Alcock [37] has determined the crystal structure of $[Me_4N]^{+}[Ph_2Pb(OAc)_3]^{-}$. The lead atom is octa-coordinated with approximately hexagonal bipyrimidal geometry. The C-Pb-C chain is linear with a Pb-C distance of 2.16 Å (normal length); the Pb-O distance is very long (2.55 Å against normally 2.20 Å).

Bürger and Biedermann [38] do not agree with the new assignments, made by S. C. Graham, Spectrochim. Acta, Part A, 26 (1970) 345, of the vibrations in the IR spectra of Me_4M (M = Sn, Pb). They provide evidence that the earlier assignments were correct.

The infrared spectrum of tetrapropynyllead is consistent with T_d symmetry [39]. Most of the spectroscopically active fundamentals have been assigned.

A complete analysis of the metal satellite NMR spectrum of tetracyclopropyllead has been carried out [40]. A correlation was found between coupling constants of various metals and hydrogen in analogous compounds; $J(M-H) = A \cdot J(M'-H) + B$.

For ^{19}F NMR spectra of fluoroaromatic organolead compounds see refs. [41], [42] and [43].

The ^{14}N NMR spectrum of trimethyllead azide [44] suggests that the α - and γ-N atoms are equivalent since the spectrum contains two peaks in an areal ratio of 2/1 at 277 and 138 ppm, respectively.

Bennett and Howard [45] studied the ESR spectrum of $Me_3PbOO^\cdot$

$$Me_3PbX + Na + O_2 \longrightarrow Me_3PbOO^\cdot + NaX$$

prepared in a rotating cryostat in cyclopropane at -196°. $Me_3PbOO^\cdot$ radicals were stable up to the boiling point of cyclopropane (-33°). There was no evidence for an equilibrium with the dimer. $Me_3PbOO^\cdot$ is more stable than the other Group IV analogues.

For photoelectron spectra of tetramethyllead see refs. [46] and [47].

NewKirk [48] has grown crystals of Group IV tetraphenyl derivatives (up to 3 cm in size) by cooling saturated solutions 0.2° per day starting from 50°. Electric, crystallographic, solubility and spectral data are reported.

Colliard and Devaud [49] studied the polarographic behaviour of triphenyllead hydroxide and diphenyllead diacetate in alcoholic media:

$$Ph_3Pb^+ + e \longrightarrow Ph_3Pb^\cdot \xrightarrow{3\,H^+ + 3\,e^-} 3\,PhH + Pb$$

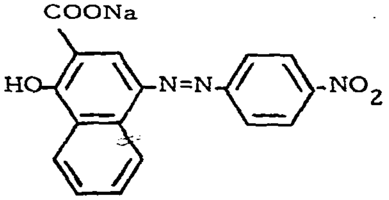
$$Ph_2Pb^{2+} + 2e^- \longrightarrow Ph_2Pb \xrightarrow{2\,H^+ + 2e^-} 2\,PhH + Pb$$

Both compounds are reduced at the mercury electrode in two successive steps. The intermediate $Ph_3Pb^{\cdot}$ and Ph_2Pb readily decompose to give side-products.

Analysis

Lead alkyls may be determined in gasoline in concentrations ranging from 1000 ppm to 1 ppb by a combination of gas chromatography and flame photometry [50]. In another method use is made of X-ray fluorescence [51]. The latter method can also be used for the determination of alkyl lead compounds in air [52].

Triethyllead salts in aqueous solution may be determined [53] spectrophotometrically by extraction with



into $CHCl_3$ at pH 8.2 and measuring the absorption at 440 nm; minimum concentration for determination is 0.5 ppm.

A complex of Bu_2Pb^{2+} with two molecules of dithizone is quantitatively extracted from aqueous solutions (pH 4.75) into toluene [54]. From the UV absorption of the complex at 485 and 610 nm the concentration of Bu_2Pb^{2+} can be calculated [55].

Toxicology

Schroeder et al [56] redetermined the oral LD_{50} of tetraethyllead for rats : 12.3 mg/kg.

McClain and Becker could not find any teratogenic effect of Me_4Pb, Me_3PbCl and Et_4Pb in pregnant rats [57].

Applications

Dick [58] incorporated Cu_2O/Ph_3PbOAc into vinyl rosin paints. Good performance after 27 months in marine environments was obtained.

According to a patent [59] the yield of acetylacetone increases when tetraethyllead is present during its preparation (heating isopropenyl acetate at 300-600°).

For the use of tetramethyllead as starting material for methyl tin compounds see Reactions, ref. [22].

REFERENCES

1 S. F. Zhil'tsov and O. N. Druzhkov, Usp. Khim., 40 (1971) 226

2 G. A. Razuvaev, V. A. Dodonov and T. G. Brilkina, Org. Peroxides, 3 (1972) 141

3 E. W. Abel, M. O. Dunster and A. Waters, J. Organometal. Chem., 49 (1973) 287

4 K. C. Williams (Ethyl Corp.), U.S. Pat., 3, 634, 481; Chem. Abstr., 76 (1972) 113375p

5 M. Boleslawski and S. Pasynkiewicz, J. Organometal. Chem., 43 (1972) 81

6 R. J. Puddephatt and G. H. Thistlethwaite, J. Organometal. Chem., 40 (1972) 143

7 E. C. Juenge, S. J. Hawkes and T. E. Snider, J. Organometal. Chem., 51 (1973) 189

8 B. C. Pant and W. E. Davidsohn, J. Organometal. Chem., 39 (1972) 295

9 L. C. Willemsens, D. de Vos, J. Spierenburg and J. Wolters, J. Organometal. Chem., 39 (1972) C61

10 D. deVos, J. Spierenburg and J. Wolters, Recl. Trav. Chim. Pays-Bas, 91 (1972) 1465

11 D. de Vos and J. Wolters, J. Organometal. Chem., 39 (1972) C63

12 J. R. Kalman, J. T. Pinhey and S. Sternhell, Tetrahedron Lett., (1972) 5369

13 U. Schöllkopf, B. Banhidai and H.-U. Scholz, Justus Liebigs Ann. Chem., 761 (1972) 137

14 A. Taberaux and R. N. Grimes, Inorg. Chem., 12 (1973) 792

15 B. Crociani, M. Nicolini, D. A. Clemente and G. Bandioli, J. Organometal. Chem., 49 (1973) 249

16 E. S. Bretschneider and C. W. Allen, J. Organometal. Chem., 38 (1972) 43

17 E. Kunze and F. Huber, J. Organometal. Chem., 51 (1973) 215

18 E. Kunze and F. Huber, J. Organometal. Chem., 51 (1973) 203

19 V. D. Mal'kov, V. P. Maslennikov and V. A. Shushunov, Zh. Obshch. Khim., 41 (1971) 1295; Chem. Abstr., 75 (1971) 87918a

20 H. Lindemann and F. Huber, Z. Anorg. Allg. Chem., 394 (1972) 101

21 H.-J. Haupt and F. Huber, Z. Naturforsch. B, 27 (1972) 724

22 Ned. Centr. Org. TNO, Neth. Appl. 7100 202; 11-7-1972; Chem. Abstr., 78 (1973) 4361b

23 S. E. Appleby, S. B. Howarth, A. T. Jones, J. H. Lippiatt, W. J. Orville--Thomas, D. Price and P. Heald, Dyn. Mass Spectrom., 1 (1970) 37; Chem. Abstr., 77 (1972) 125586s

24 K. C. Williams and D. W. Imhoff, J. Organometal. Chem., 42 (1972) 107

25 N. A. Clinton and J. K. Kochi, J. Organometal. Chem., 42 (1972) 229

26 N. A. Clinton and J. K. Kochi, J. Organometal. Chem., 42 (1972) 241

27 H. J. Haupt, F. Huber and J. Gmehling, Z. Anorg. Allg. Chem., 390 (1972) 31

28 J. Gmehling and F. Huber, Z. Anorg. Allg. Chem., 393 (1972) 131

29 T. J. Marks and A. R. Newman, J. Amer. Chem. Soc., 95 (1973) 769

30 N. Bertazzi, G. Alonzo and A. Silvestri, J. Inorg. Nucl. Chem., 34 (1972) 1943

31 M. Aritomi, Y. Kawasaki and R. Okawara, Inorg. Nucl. Chem. Lett., 8 (1972) 1053

32 J. A. Howard and E. Furimsky, J. Organometal. Chem., 46 (1972) C45

33 M. H. Abraham, J. Chem. Soc., Perkin Trans. 2, (1972) 1343

34 K. M. Gilroy, S. J. Price and N. J. Webster, Can. J. Chem., 50 (1972) 2639

35 A. S. Carson, P. G. Laye, J. A. Spencer and W. V. Steele, J. Chem. Thermodyn., 4 (1972) 783

36 J. A. McCauley and N. O. Smith, J. Chem. Thermodyn., 5 (1973) 31

37 N. W. Alcock, J. Chem. Soc., Dalton Trans., (1972) 1189

38 H. Bürger and S. Biedermann, Spectrochim. Acta, Part A, 28 (1972) 2283

39 R. E. Sacher, B. C. Pant, F. A. Miller and F. R. Brown, Spectrochim. Acta, Part A, 28 (1972) 1361

40 P. A. Scherr and J. P. Oliver, J. Amer. Chem. Soc., 94 (1972) 8026

41 W. Kitching, A. J. Smith, W. Adcock and S. Q. A. Rizvi, J. Organometal. Chem. 42 (1972) 373

42 A. N. Nesmeyanov, D. N. Kravtsov, B. A. Kvasov, E. M. Rokhlina, V. M. Pachevskaya, L. S. Golovchenko and E. I. Fedin, J. Organometal. Chem., 38 (1972) 307

43 D. N. Kravtsov, B. A. Kvasov, L. S. Golovchenko, E. M. Rokhlina and E. I. Fedin, J. Organometal. Chem., 39 (1972) 107

44 J. Müller, J. Organometal. Chem., 51 (1973) 119

45 J. E. Bennett and J. A. Howard, J. Amer. Chem. Soc., 94 (1972) 8244

46 S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner and J. P. Maier, J. Chem. Soc., Faraday Trans. 2, 68 (1972) 905

47 R. Boschi, M. F. Lappert, J. B. Pedley, W. Schmidt and B. T. Wilkins, J. Organometal. Chem., 50 (1973) 69

48 H. W. Newkirk, J. Organometal. Chem., 44 (1972) 263

49 J. P. Colliard and M. Devaud, Bull. Soc. Chim. Fr., (1972) 4068

50 P. M. Mutsaars and J. E. van Steen, J. Inst. Petrol., London, 58 (1972) 102; Chem. Abstr., 77 (1972) 22485d

51 J. M. Bills, K. S. Brier, L. G. Danko, F. J. Kristine, S. J. Turco, K. S. Zimmerman, P. M. Divelbiss and S. L. Tackett, J. Chem. Educ., 49 (1972) 715

52 K. Mizuno and H. Shiio, Bunseki Kagaku, 21 (1972) 271; Chem. Abstr., 76 (1972) 657844v

53 S. Imura, K. Fukutaka, H. Aoki and T. Sakai, Bunseki Kagaku, 20 (1971) 704; Chem. Abstr., 75 (1971) 157991v

54 F. Fauran and G. Gras, Ann. Pharm. Fr., 30 (1972) 459

55 G. Gras and F. Fauran, Ann. Pharm. Fr., 30 (1972) 545

56 T. Schroeder, D. D. Avery and H. A. Cross, Experientia, 28 (1972) 923

57 R. M. McClain and B. A. Becker, Toxicol. Appl. Pharmacol., 21 (1972) 265

58 R. J. Dick, Australas. Eng., (1969) (March) 53-6, 59-61, 63; Chem. Abstr., 77 (1972) 63431b

59 G. Künstle, H. Spes and H. Siegl (Wacker-Chemie G. m. b. H), Ger. Offen. Pat., 2, 047, 320; Chem. Abstr., 77 (1972) 100798z