

several hours. One could obtain a family of linear isotherms (with strong hysteresis), and corresponding to 2,3 or 4 h of equilibrium for each point.

The strong affinity of chloroethane for chlorinated polymers was also revealed by measurements on PVDC.

At 293 K there is adsorption (and no longer penetration) of $\text{CH}_3\text{CH}_2\text{Cl}$ and the isotherm is linear up to $p/p_0 = 0.5$, corresponding to an approximate coverage of $\theta = 2$.

The adsorption equilibrium is reached after 45 min. only but there is a strong hysteresis on desorption, indicating some kind of retention.

About 40 h of pumping were needed to clean the surface. This contrasts with the behaviour of sulfur dioxide, neopentane and butane adsorbed on PVDC in the same temperature range [1, 2] and which have surface areas similar to the surface area of chloroethane.

Conclusion. - The present study, combined with previous investigations, shows that at low temperatures PVC and PVDC may be similar because of the Cl groups present on both surfaces. At higher temperatures, however, penetration effects appear with PVC. This may be caused by the poor crystallinity of the solid, owing to its atactic structure. In the case of PVDC, on the other hand, the structure is much simpler and the crystallinity is higher. Hence, there are fewer or no penetration sites at all between the chains.

This is also in agreement with the (relatively) lower penetration of water into a chlorinated PVC (63% Cl), as observed by *Babkin & al.* [4] near room temperature.

Acknowledgments are due to Dr. *Helen Stoeckli-Evans* for X-ray photographic work and interpretations.

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191. Preparation, Properties and Structure of Phenylthionophosphine Oxide (Phenylmonothiophosphonic Anhydride), $[\text{C}_6\text{H}_5\text{P}(\text{S})\text{O}]_3$

by **J. J. Daly, L. Maier*** and **F. Sanz**

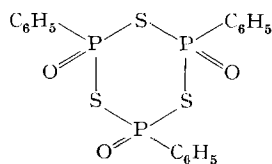
Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich, Switzerland

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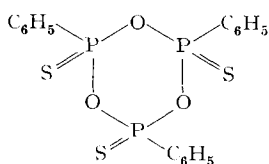
Summary. Interaction of phenylthiophosphonic dichloride with H_2S in the presence of triethylamine in benzene solution yields phenylthionophosphine oxide (I) which, in solution as well as in the solid state, is a trimer (Ib); an X-ray structural analysis indicates a nearly planar six-membered ring structure with P-O bonds in the ring.

The chemistry of dimeric thionophosphine sulfides (dithiophosphonic anhydrides) $[\text{RPS}_2]_2$ [1] and phosphonic anhydrides [2] has been studied extensively, but little is known about the preparation, structure, and properties of thionophosphine oxides.

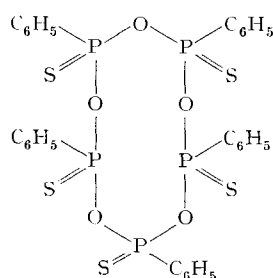
Trimeric phenylthionophosphine oxide (I) has been obtained by the reaction of phenylphosphine with SOCl_2 in benzene solution; in addition a higher polymer and phenylthiophosphonic dichloride were also formed [3]. For compound I structure Ia or Ib was proposed.



Ia



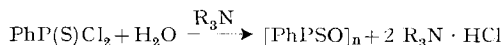
Ib



II

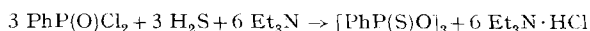
One of us argued [4] that by analogy with the structure of tetraethyl monothio-pyrophosphate, which apparently exists only in the thiono form since the thiol structure is extremely unstable, I should have structure Ib.

More recently it has been said that I is also formed in the controlled hydrolysis of phenylthiophosphonic dichloride with water in the presence of tertiary amines [5]. No physical properties nor the size of the molecule were given.



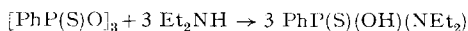
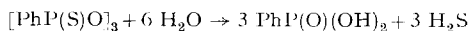
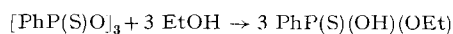
The only other paper concerned with I mentions the preparation of pentameric phenylthionophosphine oxide (II) from the interaction of $(\text{PhPO})_5$ with sulfur [6]. Again no physical properties were given. It seemed of interest to synthesize an authentic specimen of I and determine its structure unambiguously.

By analogy with dimeric thionophosphine sulfides [1], I was obtained in a fast exothermic reaction, in 44% yield, by treating a benzene solution of PhP(O)Cl_2 in the presence of a tertiary amine with H_2S . When recrystallized from hexane, I had a m.p. 135–139°.



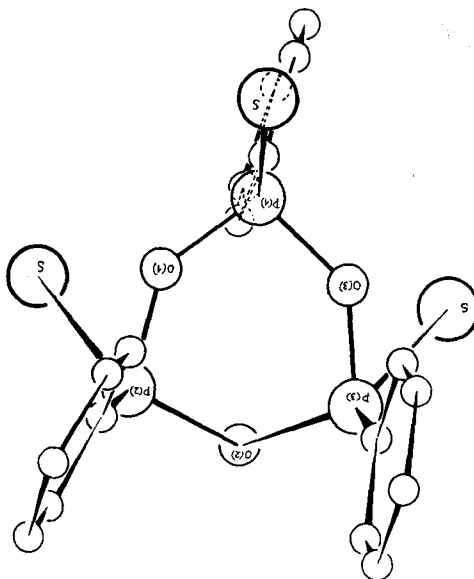
It showed in the IR. spectrum (in KBr) bands for P-S at 635.2 and 645.2 cm^{-1} and for P-O-P at 945 cm^{-1} , but no band for a P=O bond. $^1\text{H-NMR}$. (in CDCl_3): *m*- and *p*-CH at 7.55 ppm (*m*, 3.06 H); *o*-CH at 8.15 ppm (*m*, 1.94 H). ^{31}P -chem. shift (in CHCl_3): -71 ppm. Molecular weight (cryoscopically in benzene) found: 467, 442; calc. for trimer: 468.2.

The trimer I is cleaved by ethanol to give PhP(S)(OH)(OEt) , ^{31}P -78.3 ppm (ammonium salt m.p. 141–144°, ^{31}P -67 ppm); by water to give PhP(O)(OH)_2 , ^{31}P -17 ppm; and by Et_2NH to give the amide, PhP(S)(OH)NEt_2 , ^{31}P -62 ppm.



Interaction of I with PCl_5 in CCl_4 solution yields a mixture consisting of 70% PhP(S)Cl_2 and 30% PhP(O)Cl_2 . From this evidence it is concluded that I has structure Ib.

An X-ray structural analysis of single crystals of I grown from a concentrated benzene solution confirms this assignment. The crystals are monoclinic, space group $P2_1/c$ with $a = 12.257$, $b = 9.299$, $c = 21.027$ Å, $\beta = 119^\circ 46'$, $D_m = 1476$, $D_c = 1499$ kg m $^{-3}$, $Z = 4$. The structure was determined by direct methods and 3148 monochromated diffractometer data were refined by least squares to an R of 0.043. A drawing of the molecule is shown in the figure.



The molecule projected onto the least squares plane of the heterocyclic ring

The lengths of chemically equivalent bonds are in good agreement with one another, average values for the various types being P–C, 1.879(3); P=S, 1.896(1); P–O, 1.613(3) Å; C–C, 1.383(6); C–H, 1.02(6) Å. The heterocyclic ring is approximately planar, the deviations of the individual atoms from its least squares (w = atomic number) plane are P(1), -0.053 ; O(1), 0.044 ; P(2), 0.061 ; O(2), -0.228 ; P(3), 0.060 ; O(3), 0.048 Å. Two sulfur atoms and one phenyl group lie on one side of this plane while the other sulfur atom and the remaining two phenyl groups lie on the other side. This suggests the possible existence of another isomer with all three sulfur atoms lying on the same side of the heterocyclic ring. The P–O bond length of 1.613 Å, which is the same as that found in the bridge bond of pyrophosphates, suggests that ring formation does not lead to any additional π -stabilisation. The near planarity of the heterocyclic ring is probably the result of intramolecular repulsions involving the sulfur atoms and the phenyl groups.

The method of preparation has been extended to the cyclohexyl (m.p. 159 – 161°) and the methyl (m.p. 118 – 123°) derivatives.

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192. Struktur von Coleon E, einem neuen diterpenoiden Methylenchinon aus der *Coleus barbatus*-Gruppe (*Labiatae*)

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Summary. We have isolated from the glands on the leaves of *Coleus barbatus* (Benth.) Agnew, *C. kilimandschari* (Gürcke) Agnew and a *C. species* P.R.O. Bally No. 10431, all of East African origin, a new, very labile, deeply red coloured quinone methide, Coleon E, C₂₀H₂₂O₅. Degradations and spectra (including ¹³C-NMR.) have been interpreted in terms of the unusual irregular diterpenoid structure **1**. Its fully conjugated unsaturated system extends over 3 rings. The CH₃-group at C(3) and *n*-propyl side chain at C(13) instead of the usual isopropyl group are regarded as arising by modification of an abietane precursor. *Coleon E*, after reduction and methylation, has been found to undergo a skeletal rearrangement leading to a formal interchange of the alkyl side chain with a phenolic OH-group.

Einleitung. – Als Coleon E bezeichnen wir ein neues diterpenoides *p*-Methylenchinon, das in bedeutender Menge in Blattdrüsen von Spezies der ostafrikanischen *Coleus barbatus*-Gruppe vorkommt. Muster dieser Arten hatten wir schon seit mehreren Jahren untersucht²⁾, ohne dass es uns gelungen war, die genuinen Farbstoffe kristallisiert und rein zu erhalten. Ihre ausserordentliche Empfindlichkeit erschwerte die genauere Untersuchung. Zahlreiche Reaktionen mussten deshalb an amorphem, chromatographisch soweit wie möglich gereinigtem Material ausgeführt werden. Erst vor kurzem gelang es uns, den Hauptfarbstoff (= Coleon E) zu kristallisieren. Besonders reich daran ist *C. kilimandschari* (Gürcke) Agnew³⁾, ein aufrechter, dicht flaumhaariger, fast baumartiger Strauch mit eiförmig bis eiförmig-elliptischen Blättern, endständigen Blütentrauben und hellviolett-blauen Blüten. Er kommt im höher gelegenen Buschland von Kenya vor. Im Gebiet der Kikuyus wird er, da rasch wachsend, zur Herstellung von Hecken benutzt.

Sehr ähnlich ist *C. barbatus* (Benth.) Agnew, ein ebenfalls aufrechter, sukkulenter, dichtwollig behaarter Strauch. Von *C. kilimandschari* unterscheidet er sich durch die

¹⁾ Aus der Dissertation von P. Rüedi, Universität Zürich; in Vorbereitung.

²⁾ Vorarbeiten haben die Herren H.-P. Küng (1959) und M. Ribi (1967) ausgeführt.

³⁾ *Coleus kilimandschari* ist früher von *C. barbatus* nicht unterschieden worden. Dr. A. D. Q. Agnew, University College of Wales, Dept. of Botany, Aberystwyth, vereinigt neuerdings in «Revision of the Labiatae», «Flora of the Herbs of Upland Kenya», Oxford University Press, Nairobi (im Druck), zahlreiche *Coleus*-Arten mit dem Genus *Plectranthus* l'Hérit. Die oben angeführten Angaben über *C. kilimandschari* und *C. barbatus* sind seiner Flora entnommen.